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Chemistry. — *Membrane and Osmosis.* V. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of January 25, 1930.)

Osmosis of binary liquids through a membrane $M(n)$.

In Comm. M.O. III we have discussed some phenomena, which may occur with the diffusion through a membrane $M(W)$ (positive and negative osmosis, etc.); we deduced them with the aid of the O.W.A. of the liquids and also with the aid of the W-amount which these liquids give to the membrane. We found among other things:

A_1. when two liquids give a different W-amount to a membrane $M(W)$, the water will diffuse from the liquid giving the greater W-amount to the membrane, towards the liquid giving the smaller W-amount to this membrane.

If we consider the W-amount of the two boundary planes of the membranes, then we can say also:

A_2. the water diffuses in a membrane $M(W)$ from the boundary plane having the greater W-amount, to the boundary plane having the smaller W-amount.

Now we shall say:

A_3. in a membrane $M(W)$ the water runs "downward"; or: in a membrane $M(W)$ is a "down W-current".

As this result obtains not only for water, but also for every other substance, we consequently have in general:

B. in a membrane permeable for one substance only, this substance runs downward; or: in a membrane permeable for one substance only is a downcurrent.

Instead of a membrane, permeable for one substance only, we now take a membrane $M(n)$; on one boundary plane it will get a certain amount of the substances W, X, Y etc. and on the other boundary plane a certain different amount of these substances. If we now assume that each of these substances runs downward in this membrane also, then we should have:

C_1. in a membrane $M(n)$ all substances run downward; or: in a membrane $M(n)$ all currents are downcurrents.

It is evident that these various downcurrents need not have the same direction; e.g. when the left side boundary plane has a greater W- but a smaller X-amount than the right side one, then the down W-current will go towards the right and the down X-current towards the left.

In Comm. M.O. III we have deduced what was said above sub B; as we shall see later on, however, this deduction does not obtain any longer for a membrane $M(n)$. Instead of C_1 we might also assume now that one (or more) of the substances passes through the membrane in the opposite direction, viz. from the boundary plane in which this substance has the smaller W-amount towards the boundary plane in which this substance has the greater W-amount. Then we shall say: this substance runs upward, or there is an upcurrent. Instead of C_1 we should then have:

C_2. in a membrane $M(W)$ one or more of the substances can also run upward; or also: there may be one or more upcurrents in a membrane $M(n)$.

We may summarise all that has been discussed above, also by saying:

D. when there is only one current in a membrane, this will be a down current; when there are more currents, then there may be upcurrents also.

We shall refer to this later on.

We now consider the osmotic system:

$$L \mid M(n) \mid L' \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

in which L and L' are binary liquids; we imagine them represented by two points on line WX of figs. 1—4; for the sake of concentration we suppose as we did also in Comm. M. O. IV that in these figures the left side liquid L of system (1) is also situated on the left side of liquid L'. The figs. 1—4 of this communication are the same as the figs. 1—4 of Comm. M.O. I; the fully drawn curve $W'X$ is the W-curve and the dotted curve WX' the X-curve of the membrane $M(n)$.

In Comm. M.O. IV we have seen that with the osmosis in system (1) the *D.T.*'s *a*, *b* and *c* of scheme I and the transition-*D.T.*'s *e* and *f* of scheme II can occur; the *D.T.*'s between parentheses are not possible.

SCHEME I.

	W	X
a.	← 0	← (cond.)
b.	→	←
c.	→	→ 0 (cond.)
d.	[← 0	→ 0]

SCHEME II.

	W	X
e.	—	←
f.	→	—
g.	[—	→ 0]
h.	[← 0	—]

In Comm. M.O. IV we have deduced this with the aid of the O.W.A. and O.X.A. of the liquids; we can also deduce this now with the aid of the W- and the X-amount which these liquids give to the boundary plane of the membrane.

We then begin by assuming that C_1 obtains viz. that W and X run downward, so that there are only downcurrents in the membrane.

We now take the osmotic system:

$$\left.\begin{array}{cc} a_1 \mid M(n) \mid a_2 & \text{fig. } 1 \\ \longrightarrow W \qquad \longleftarrow X & \text{D.T. } b \end{array}\right\} \quad . \; . \; . \; . \; . \quad (2)$$

This means that we have a membrane $M(n)$, the W- and X-curves of which are represented by fig. 1 ; the two liquids a_1 and a_2 are represented by the points a_1 and a_2 of this same figure 1. The arrows indicate the directions in which the substances diffuse.

The left side liquid a_1 namely gives a greater W-amount to the membrane than the right side liquid a_2 (viz. $a_1 w_1 > a_2 w_2$). If we now assume that a boundary plane is approximately in equilibrium with the liquid, then the left side boundary plane will consequently get a greater W-amount than the right side one ; so the water will now run from left to right.

The liquid a_1 gives a smaller X-amount to the membrane than the liquid a_2 (viz. $a_1 x_1 < a_2 x_2$) ; so the substance X diffuses from a_2 towards a_1, consequently towards the left.

It appears from scheme I that the osmosis now takes place according to the congruent $D.T.b$. From this follows :

when the W- and X-curves of a membrane are represented by fig. 1, then the osmosis takes place according to the congruent $D.T.b$ of scheme I.

We now take as a special case of (2) the system :

$$\left.\begin{array}{lll} \multicolumn{2}{c}{\textit{water} \mid M(n) \mid L'} & \text{fig. } 1 \\ \longrightarrow W & \longleftarrow X & \text{D.T. } b \end{array}\right\} \quad . \; . \; . \; . \; . \quad (3)$$

We now see that the water diffuses towards the liquid and the substance X from the liquid towards the water ; consequently both liquids run through the membrane congruently.

We now take the osmotic system

$$\left.\begin{array}{lll} \multicolumn{2}{c}{a_1 \mid M(n) \mid a_2} & \text{fig. } 2 \\ \longleftarrow 0\, W & \longleftarrow X & \text{D.T. } a \end{array}\right\} \quad . \; . \; . \; . \; . \quad (4)$$

in which $M(n)$ now is a membrane, of which the W- and X-curves are represented by fig. 2 ; again the arrows indicate the direction in which the substances diffuse.

It appears namely from fig. 2 that the liquid a_1 now gives a smaller W- and a smaller X-amount to the membrane than the liquid a_2 (viz. $a_1 w_1 < a_2 w_2$ and $a_1 x_1 < a_2 x_2$) ; so the water and the substance X now both diffuse from a_2 towards a_1, consequently towards the left. Now the osmosis takes place according to the mixed $D.T.$ of scheme I. The water now diffuses incongruently, as the sign o with the arrow indicates also.

We now substitute for the liquid a_2 of system (4) the liquid a_4 of fig. (2) ; we then get the osmotic system :

$$\left.\begin{array}{lll} \multicolumn{2}{c}{a_1 \mid M(n) \mid a_4} & \text{fig. } 2 \\ \longrightarrow W & \longleftarrow X & \text{D.T. } b \end{array}\right\} \quad . \; . \; . \; . \; . \quad (5)$$

The liquid a_1 namely gives a greater W-amount to the membrane than the liquid a_4 (viz. $a_1 w_1 > a_4 w_4$) ; the liquid a_1, however, gives a smaller

X-amount to the membrane than the liquid a_4 (viz. $a_1 x_1 < a_4 x_4$). So the substances diffuse in the direction of the arrows viz. according to the congruent *D.T.b* of scheme I.

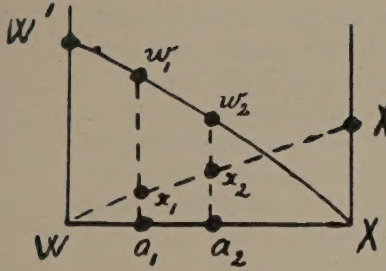

Fig. 1.

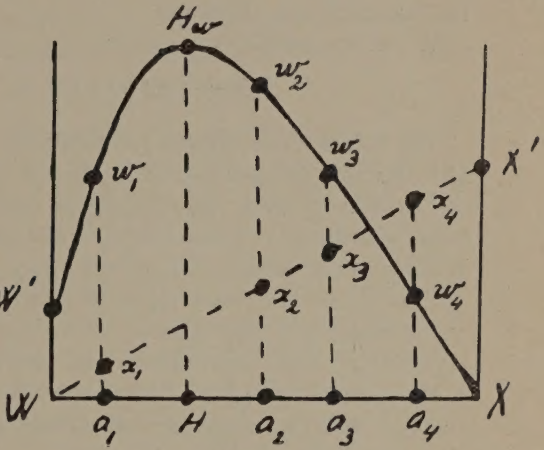

Fig. 2.

If we substitute for the liquid a_4 the liquid a_3 of fig. 2, we get the osmotic system :

$$\left.\begin{array}{lll} a_1 \mid M(n) \mid a_3 & & \text{fig. } 2 \\ \text{——} W & \longleftarrow X & \text{D.T. } e \end{array}\right\} \quad \ldots\ldots \quad (6)$$

As the liquids a_1 and a_3 give the same W-amount to the membrane (viz. $a_1 w_1 = a_3 w_3$), no water will now consequently run through the membrane. So the substances now diffuse according to the transition *D.T.e* of scheme II.

It is easy to see now : when in fig. 2 we take two arbitrary liquids L and L', then the osmosis will always take place according to one of the *D.T.*'s *a* or *b* or according to the transition *D.T.e* ; so we may say :

when the W- and X-curves of a membrane are represented by fig. 2, then the substance X will always diffuse congruently ; the water, however, can diffuse as well congruently (*D.T.b*) as incongruently (*D.T.a*).

As a special case we now take the systems :

$$\left.\begin{array}{lll} \text{water} \mid M(n) \mid L'(a_4 X) & & \text{fig. } 2 \\ \longrightarrow W & \longleftarrow X & \text{D.T. } b \end{array}\right\} \quad \ldots\ldots \quad (7)$$

$$\left.\begin{array}{lll} \text{water} \mid M(n) \mid L'(W a_4) & & \text{fig. } 2 \\ \longleftarrow 0\, W & \longleftarrow X & \text{D.T. } a \end{array}\right\} \quad \ldots\ldots \quad (8)$$

In them L' $(W a_4)$ represents a liquid between the points W and a_4 and L' $(a_4 X)$ a liquid between the points a_4 and X in fig. 2. If in this figure we suppose $WW' = a_4 w_4$, we find that the arrows in (7) and (8) indicate the direction in which the substances diffuse. So we find :

when the W- and X-curves of a membrane are represented by fig. 2 the water may diffuse as well from the water towards the liquid as from the liquid towards the water.

We now consider the system :

$$\textit{water} \mid M(n) \mid L' \qquad \text{fig. 2} \quad \ldots\ldots\ldots \quad (9)$$

The substance X diffusing towards the water, as is shown by (7) and (8), this now changes into an X-containing liquid. If, however, we suppose the quantity of water very large with respect to the quantity of L' or this water substituted continuously by other water, we may assume that on the left side of the membrane practically pure water is found continuously.

If we leave the system to itself now, then the liquid L', giving off X continuously, will also pass at last into a liquid, practically consisting of pure water ; so in fig. 2 the liquid L' moves towards point W.

We now imagine for L' in (9) a liquid, situated in fig. 2 between a_4 and X ; then the substances will diffuse as in system (7) ; the water will then run towards the liquid.

As soon as L' has passed the point a_4, however, and is situated, therefore, between W and a_4, the substances will diffuse as in system (8) ; then the water runs from the liquid towards the water.

From this appears :

in the beginning of the osmosis water diffuses towards the liquid ; after some time water diffuses away from the liquid towards the pure water.

Later on we shall see that these phenomena may occur, when the liquid L' consists of water and tartaric acid.

We now consider the osmotic system :

$$\left.\begin{array}{lll} \textit{water} \left| \dfrac{M_1(n)}{M_2(n)} \right| L'(Wa_4) & & \\ M_1(n) \longrightarrow W & & \longleftarrow X \\ M_2(n) \longleftarrow 0\,W & & \longleftarrow X \end{array}\right\} \quad \ldots\ldots \quad (10)$$

in which two membranes, which can function independently from one another ; we imagine the W- and X-curves of the membrane $M_1(n)$ represented by fig. 1 and those of the membrane $M_2(n)$ by fig. 2 ; the liquid L' is represented by a point between W and a_4 in fig. 2 ; the arrows indicate the directions in which the substances diffuse in this system.

We now can regulate the surfaces of both membranes at every moment in such a way that as much water runs towards the left as towards the right ; this combination of both the membranes then behaves as a membrane, permeable for X only. Later on we shall see that this is possible when the liquid L' consists of water + tartaric acid ; a combination of two membranes, one consisting of cellophane and the other of pig's bladder, can behave as a membrane, permeable for tartaric acid only.

In the osmotic system :

$$\left.\begin{array}{lll} L \mid M(n) \mid L' & & \text{fig. 3} \\ \longrightarrow W & \longleftarrow X & \text{D.T. } b \\ \longrightarrow W & \longrightarrow 0\,X & \text{D.T. } c \end{array}\right\} \quad . \; . \; . \; . \; . \; (11)$$

is a membrane, the W- and X-curves of which are represented in fig. 3.

It appears from the shape of the W-curve that water must always diffuse towards the right now ; it follows from the shape of the X-curve that the substance X can run through the membrane as well towards the left as towards the right. Now the osmosis may take place either according to the congruent *D.T.b* or according to the mixed *D.T.c* or according to the transition *D.T.f*. It depends upon the compositions of the liquids L and L' which of these *D.T.'s* will occur ; when both liquids are situated between W and U, the *D.T.b* occurs ; when both liquids are situated between U and X, the *D.T.c* occurs ; when, however, L is situated between W and U and L' between U and X, then both *D.T.s* are possible.

In the osmotic system :

$$\left.\begin{array}{lll} L \mid M(n) \mid L' & & \text{fig. 4} \\ \longleftarrow 0\,W & \longleftarrow X & \text{D.T. } a \\ \longrightarrow W & \longleftarrow X & \text{D.T. } b \\ \longrightarrow W & \longrightarrow 0\,X & \text{D.T. } c \end{array}\right\} \quad . \; . \; . \; . \; . \; (12)$$

is a membrane, the W- and X-curves of which are represented by fig. 4.

It is easy to find now that the osmosis may take place according to one of the *D.T.'s a, b* and *c* or according to one of the transition *D.T.'s* e or *f* ; of course it depends upon the composition of the two liquids, which of these *D.T.'s* will occur.

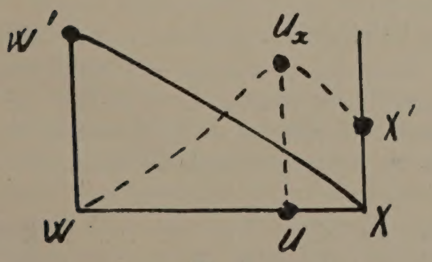

Fig. 3.

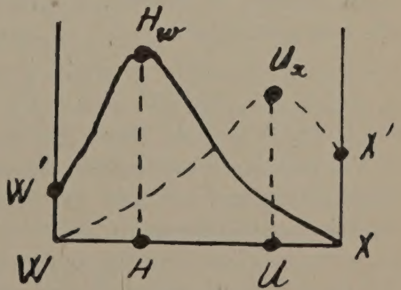

Fig. 4.

In Comm. M. O. IV we have deduced, with the aid of the O.W.A. and O.X.A. of the liquids, that the *D.T.'s a, b* and *c* of scheme I are possible ;

in this communication we found the same with the aid of the *W*- and the *X*-amount the liquids give to the membrane. It also became clear from this that when in the membrane of a system only downcurrents occur, the *D.T.* of a system will follow from the *W*- and *X*-amount the liquids give to the membrane, consequently from the *W*- and *X*-curves of the membrane.

If, however, we omit this restriction and if we assume, therefore, that also upcurrents may occur, then it is clear that the three *D.T.*'s *a*, *b* and *c* still remain possible; then, the *D.T.* of a system, however, can no longer be deduced from the *W*- and *X*-curves of its membrane.

In order to illustrate the above, we shall first consider one more system, in which only a single substance diffuses. For this obtains what was said in A_3 or B viz.: in a membrane, permeable for one substance only is a downcurrent. In order to deduce this in a way differing a little from the one we applied before, we take the system:

$$n \times L \mid \qquad \mid n' \times L' \quad \ldots\ldots \quad (13)$$

in which the liquid may contain an arbitrary number of substances; for the sake of concentration we assume that L gives a greater *W*-amount to the membrane than the liquid L'. The boundary planes of the membrane have been indicated by the vertical lines.

We now imagine the right side boundary plane shut off by an impermeable wall; we then represent this system by:

$$n \times L \mid \quad u \quad \| \, n' \times L' \quad \ldots\ldots \quad (14)$$

in which u is the *W*-amount the membrane gets in the liquid L; when there are m quantities of this membrane, this will contain mu mol. of water.

If we now place the impermeable wall on the left side of the membrane, then so much water will run from the membrane towards the right till the right side liquid is in equilibrium with the membrane. As this right side liquid changes its quantity and its composition in this way, we represent the new system by:

$$n \times L \, \| \quad u'_1 \quad \mid n'_1 \times L'_1 \quad \ldots\ldots \quad (15)$$

in which u'_1 is the *W*-amount the membrane gets in the new right side liquid L'_1. The right side liquid now has taken up $m\,(u—u'_1)$ mol. *W*.

We now place the impermeable wall once more on the right side of the membrane, water will now run from the liquid L towards the membrane; we then get the system:

$$n_1 \times L_1 \mid \quad u_1 \quad \| \, n'_1 \times L'_1 \quad \ldots\ldots \quad (16)$$

in which u_1 is the *W*-amount the new left side liquid L_1 gives to the membrane. So the left side liquid has given off $m(u_1—u'_1)$ mol. *W* to the membrane. We now find: with the transition of (14) into (16):

liquid L has given off $m\,(u_1 - u'_1)$ mol. W
liquid L' has absorbed $m\,(u - u'_1)$ mol. W.

The remainder, after subtracting these quantities viz. $m(u—u_1)$ mol. *W* has been given off by the membrane.

If we take m small with respect to n and n', then L, u and L' of system (14) differ only a little from L_1, u_1 and L'_1 in (16).

If we call the transition of the water, mentioned above, a "sluice current", then we may say therefore :

E_1. the sluice current takes the water from the liquid, giving the greatest W-amount to the membrane, towards the liquid, giving the smallest W-amount to this membrane.

Consequently we may say also :

E_2. the sluice current takes the water in the same direction as a membrane, in which the water runs downward.

As the sluice current is always possible, follows :

E_3. in a membrane $M(W)$ a downcurrent is always possible.

As with the diffusion of water only two directions can be imagined however, one of which is impossible, follows :

E_4. in a membrane $M(W)$ the water must run downward.

We now imagine a membrane $M(n)$ in system (14) instead of a membrane $M(W)$; this will then get a definite W-, X-, Y-amount, etc. By moving the impermeable wall we then get once more the corresponding systems (15) and (16). Instead of E_1 we now have :

F_1. the sluice current takes every substance from the liquid, giving the greater amount of this same substance to the membrane, towards the liquid giving the smaller amount of this substance to the membrane.

So it depends upon the absorption of the membrane whether this sluice current will take all substances in the same direction, or some substances towards the left and other substances towards the right.

Instead of E_2 we now have :

F_2. the sluice current takes all substances in the same direction as a membrane in which all substances run downward.

As the sluice current is always possible, it follows :

F_3. in a membrane $M(n)$ a *D.T.* is possible in which all currents are downcurrents.

Consequently a complete analogy exists as far as this between the membranes $M(W)$ and $M(n)$. If now there were only two *D.T.'s*, one of which should be impossible, then in accordance with E_4 we might conclude also : in a membrane $M(n)$ only downcurrents are possible ; as, however, more *D.T.'s* are possible (viz. the congruent one and the several mixed ones) we may not draw this conclusion. So these considerations do not raise any objection to the assumption :

F_4. in a membrane $M(n)$ upcurrents may occur as well as downcurrents.

Reversally it does not follow from this of course that upcurrents can occur in reality ; we shall refer to this later on.

(To be continued.)

Leiden, Lab. of Inorg. Chemistry.

Physics. — *Continued investigations on the luminescence from solidified gases at the temperature of liquid helium.* By L. VEGARD and W. H. KEESOM. (Abstract of Communication N⁰. 205*b* from the Physical Laboratory at Leiden.)

Communicated at the meeting of January 25, 1930.

§ 1. The present paper is intended to give a summary account of results of experiments, which with the assistance of Cand. Real. LEIV HARANG were carried out at the Physical Laboratory of Leiden during the spring and summer of 1927 and 1928. The object of these experiments was to extend in various directions our knowledge of the luminescence spectra emitted when solidified gases are bombarded with electric rays. Results of experiments undertaken during the same period at the temperature of liquid hydrogen were recently published by one of us in two parts, one of which (Comm. N⁰. 200) deals with the luminescence produced by cathode rays, and a second part (Comm. N⁰. 205*a*) with luminescence produced by canal rays.

The present paper deals with luminescence from solid nitrogen and nitrogen-neon mixtures produced by cathode rays of high velocity at the temperature of liquid helium.

The object of the experiments was mainly the following:

1. To obtain spectra of the afterglow which might be compared with spectra from direct light taken under the same conditions.

2. To take spectra with a big spectrograph from STEINHEIL in order to improve our wavelength measurements.

3. To study the luminescence in the ultraviolet with a quartz spectrograph of fairly high dispersion.

The afterglow spectra were taken by means of the phosphoroscope described by one of us in Comm. N⁰. 200. For the study of the afterglow spectra in the visible part we used the small spectrograph which was used in previous investigations of this kind. The spectra in the ultraviolet were studied by means of a big quartz spectrograph kindly lent us by Professor W. J. DE HAAS.

With regard to the experimental procedure we may refer to previous publications (Comm. N⁰. 175, N⁰. 183, N⁰. 186).

The spectra obtained are given in the two plates reproduced at the end of the paper, together with tables which give the most important data for each spectrogram.

Spectrograms denoted by (*b*) correspond to the afterglow, all others to direct light emitted during ray bombardment.

All the spectrograms were measured in Oslo with the assistance of Mr. S. STENSHOLT and Mr. S. VEDØ.

Wavelength tables corresponding to each spectrogram together with a more detailed discussion will appear in a more extensive paper, which will appear in the Communications of the Leiden Laboratory. In this abstract we only intend to give a short description of the most important facts and consequences.

Results obtained with the small glass spectrograph.

§ 2. Reproductions of the spectra obtained with the small glass spectrograph are given on Pl. I N⁰. 3—12. Spectrogram Pl. I N⁰. 5 is taken through a double Nicol prism, and it shows that the luminescence is not polarized to any noticeable degree.

With regard to the bands N_1, N_2, N_3 and N_4 it is of interest to notice the following facts:

1. All four bands appear in the afterglow.
2. Previous results (Comm. N⁰. 183) regarding the motion and contraction of N_1 have been confirmed. When the nitrogen concentration approaches zero, the wavelength of N_1 approaches a value, for which our present experiments give the average value 5577.2, which within the limit of error coincides with the wavelength of the green auroral line.
3. For small nitrogen concentrations N_3 appears strong, especially in the afterglow spectrum, which in the red and green part only gives the N_1-, N_2-, N_3- and N_4-bands with wavelengths 5577.2, 5205, 6325, 5947 respectively. But we have to remember that N_2 under other conditions may have components between 5220—5240.

These four bands coincide within the limits of present accuracy with the four principal lines in the red and green part of the auroral spectrum.

In addition to these four bands the spectrograms contain lines belonging to the series C, η, (ε), α, ζ, b' and perhaps χ.

Results obtained with the big STEINHEIL *spectrograph.*

§ 3. Two exposures were made at the liquid helium temperature with the STEINHEIL spectrograph, but only one of the spectrograms (Pl. I N⁰. 13) was of any value.

Some twenty lines and bands could be measured.

The interest attached to these results is first of all that a number of lines, — with the exception of N_1, which is very diffuse and faint — have been measured with a very much higher accuracy than before, but secondly a particular importance is attached to the N_2-band.

The band is seen to consist of two parts, one consisting of a diffuse band with two maxima (5209, 5202) stretching across the spectrum, and the other of a short band restricted to the middle part of the spectrum and consisting of four maxima (5243, 5236, 5229, 5221). Pl. II N⁰. 14 shows an enlarged reproduction of these bands.

The spectrum is formed by throwing an image of the luminous surface on the slit. The curious form of the spectrum of N_2 means that the conditions under which light is excited in the middle part of the spectrum is different from those of the surroundings. According to the experimental conditions the N_2-band may consist of two groups of bands, one near 5206, another near 5235. As pointed out by one of us [1]), similar variations seem to exist for the second green auroral line.

Spectrograms taken with the big quartz spectrograph.
Pl. I N⁰. 1 and 2, and Pl. II.

§ 4. The lines identified belong to the following series:

η, ε, a, ζ, b', B, D, d, F, f and perhaps $\mathscr{H}$.

The η-series.

§ 5. For systems with small nitrogen concentrations the η-series is split up into a number of component series. The whole system of lines satisfies an equation of the form:

$$\nu_{m,s} = \nu_{0,s} - T_1(m_1), \quad \ldots\ldots\ldots \quad (1)$$

where $T_1(m_1)$ is the bottom term of the ε-system:

$$T_1(m_1) = 2323.3\, m_1 - 14.898\, m_1^2.$$

$\nu_{0,s}$ has the values given in table I.

TABLE I.

s	$\nu_{0,s}$	$\Delta\nu_{0,s}$
1	47190	3 × 34
2	47291	2 × 32
3	47354	36
4	47390	39
5	47429	46
6	47475	2 × 38
7	47551	30
8	47581	

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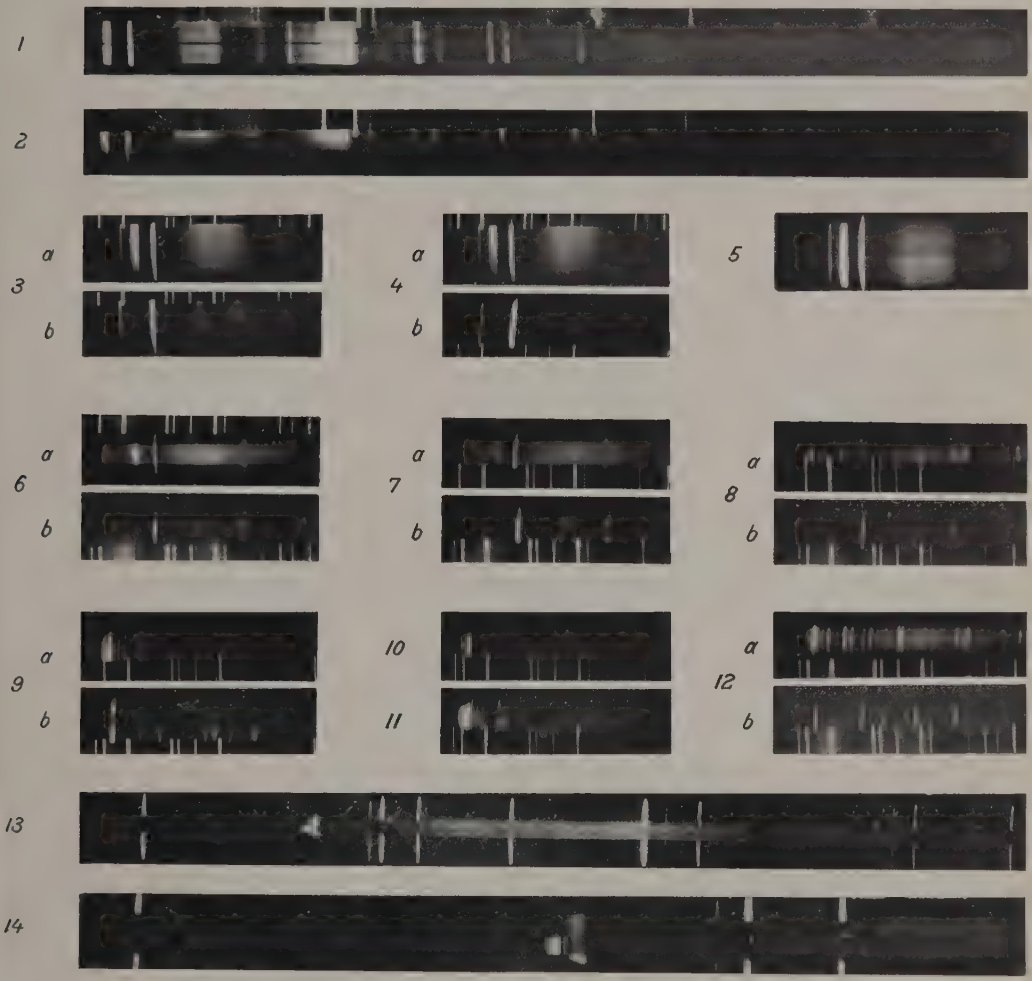
[1]) L. VEGARD, Naturwissenschaften **17**, 980, 1929.

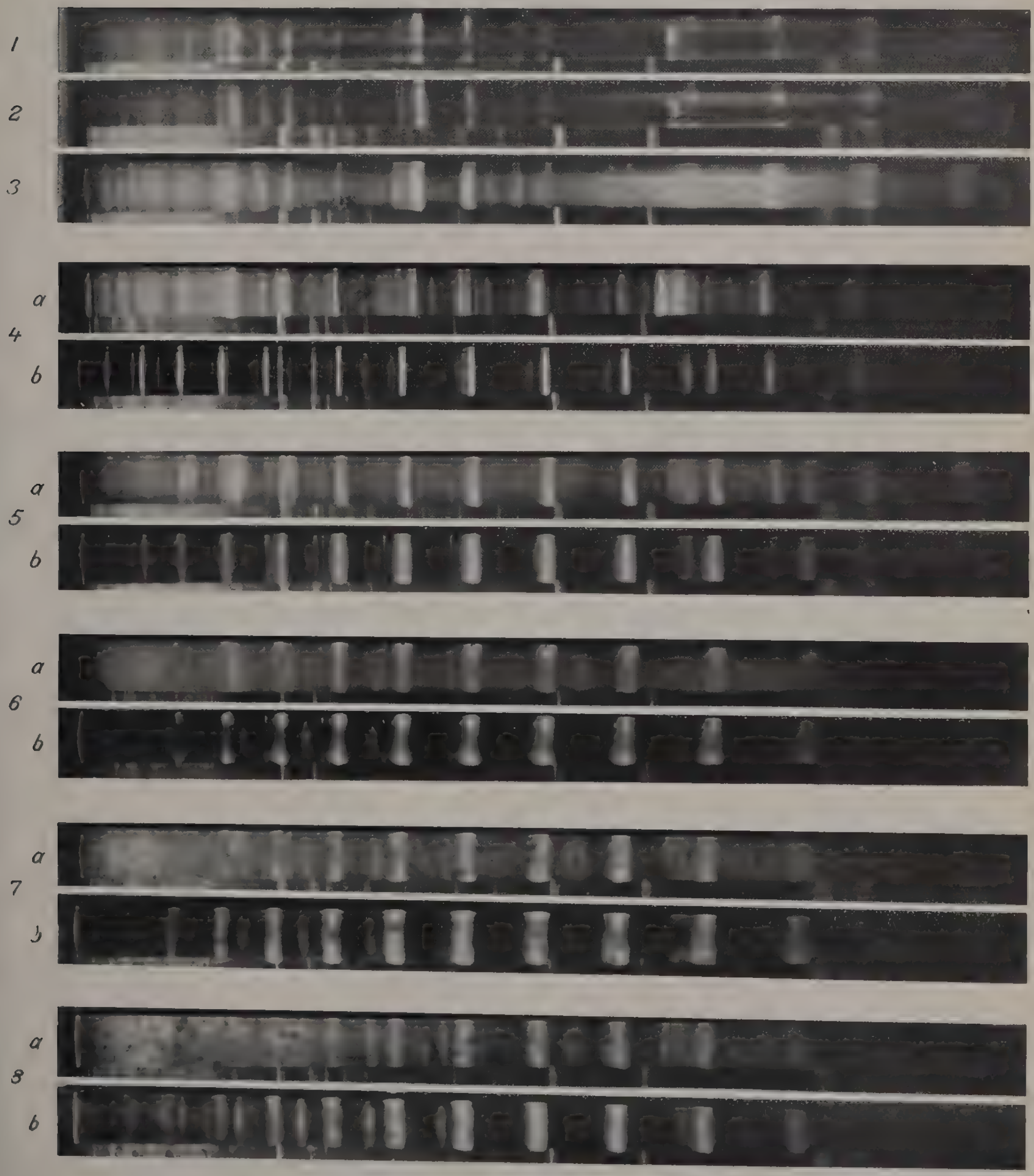
L. VEGARD AND W. H. KEESOM: CONTINUED INVESTIGATIONS ON THE LUMINESCENCE FROM SOLIDIFIED GASES AT THE TEMPERATURE OF LIQUID HELIUM.

PLATE I.



L. VEGARD AND W. H. KEESOM: CONTINUED INVESTIGATIONS ON THE LUMINESCENCE FROM SOLIDIFIED GASES AT THE TEMPERATURE OF LIQUID HELIUM.

PLATE II.



The frequency differences $\triangle \nu_{0.s}$ appear to be nearly multipla of some principal frequency equal to about 36 cm^{-1}.

As pointed out in previous papers by one of us [1]) the multiplicity is explained as being due to vibrations of the molecular elements of the crystal lattice.

The other lines of the ε-system originating from higher oscillatory levels are faint and especially very faint in the afterglow spectrum.

The a-series.

§ 6. The *a*-series consists of doublets with constant frequency intervals between the components. The two series *a*, *a′* are represented by the formula:

$$\nu_{\alpha} = \nu_{\alpha'} - 69 = 39892 - 1927.3\, n + 14.75\, n^2 \quad . \quad . \quad . \quad . \quad (2)$$

This formula is very nearly identical with the one deduced from observations at liquid hydrogen temperature for argon containing small quantities of nitrogen, and there is no doubt that in both systems we are dealing with essentially the same series, and that it must originate from nitrogen, which is the substance common to both systems.

The b′-series.

§ 7. The *b′*-series is found to be closely related to the *b*-series and the *B*-system described by one of us in a previous paper (Comm. N⁰. 200). In the case of the *b′*-series we have observed no less than 10 lines, and as they are fairly sharp, the series formula may be deduced with considerable accuracy. It now appears that the *b′*-series is closely related to the ε-system, and in a way expressed by the relation:

$$\nu_{b'} = 48860 - T_1\,(m_1), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $T_1(m_1)$ is the bottom term of the ε-system. Now the *b′*-series and the *b*- and *B*-systems are connected by the relations:

$$\nu_{b'} = \nu_{b\,(I)} - 94 = \nu_{B\,(I)} + 76, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When we take into account the oscillations of molecular elements, it is possible, that the *B*-, *b*-, *b′*- and ε-systems only differ from one another by differences of the quantum numbers of molecular vibrations.

The D- and d-series.

§ 8. The *D*-series was observed at the liquid hydrogen temperature and described in Comm. N⁰. 200. At the temperature of liquid helium more lines were observed, and they could be more accurately measured. The frequencies are given by the formula:

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[1]) L. VEGARD, Nature **125**, 14, 1930. Naturwissenschaften, **18**, 67, 1930. Det Norske Vid. Akad. Avh. I Nr. **2**, 1930.

$$\left.\begin{array}{l}\nu_D = 47150 - T_1(m_1) \,, \\ \qquad\qquad\qquad m_1 = 3,\ 4,\ \ldots\ 11\end{array}\right\} \quad \ldots \quad (5)$$

where $T_1(m_1)$ is the bottom ε-term, showing the close relation between the *D*-series and the ε-system.

The *d*-series, which is closely connected to *D*, can be expressed by the formula:

$$\left.\begin{array}{l}\nu_d = 45026 - T_1(m_1) \,. \\ \qquad\qquad\qquad m_1 = 3,\ 4,\ \ldots\ 9\end{array}\right\} \quad \ldots \quad (6)$$

The *D*- and *d*-series have the same bottom levels as the ε-system, but seem to have an upper level system of their own. Both the *D*- and the *d*-series appear strong in the afterglow.

The F- and f-series.

§ 9. Both *F* and *f* are doublet series with the same frequency difference between the components equal to 52 cm^{-1}.

The observed wavelength and frequency of the observed lines are given in the tables II and III. Both series are closely related to the *D*-series, for

TABLE II.
The F—F'-series

m_1	Observed			
	λ	ν	$\Delta\nu$	$\nu_F - \nu_{F'}$
5	2785.1	35905		
			2028	
4	2640.3	37874		59
	2636.2	37933		
			2032	
3	2505.3	39915		50
	2502.2	39965		
			2043	
2	2383.2	41960		48
	2380.5	42008		
			2033	
1	2270.6	44041		
			2029	
0	2176.6?	45943		(127?)
	2170.6?	46070		
			Mean: 52	

TABLE III.
The f—f'-series

m_1	Observed			
	λ	ν	$\Delta\nu$	$\nu_f - \nu_{f'}$
9	3636.9	27496		
			2018	
8	3388.4	29514		
			2077	
7	3170.4	31542		49
	3165.5	31591		
			2077	
6	2974.8	33616		52
	2970.2	33668		
			2120	
5	2798.0	35740		48
	2794.2	35788		
			2143	
4	2640.4	37873		58
	2636.4	37931		
			2152	
3	2494.8?	40083		
			Mean: 52	

we find that D_8 ($\lambda = 3388$) is identical with one of the F-lines, and D_5 ($\lambda = 2785$) is identical with one of the f-lines.

The F- and f-series should therefore be closely related to one another, and this is confirmed by the fact that one doublet (2640, 2636) is common to both the F- and the f-series.

These relations would indicate that not only D and d, but also F and f are formed by jumps to the bottom atomic vibrational levels of the ε-system. But the series differ as regards the quantum numbers of molecular oscillations.

Doublets in the spectrum of direct light from pure neon.

§ 10. On the spectrograms for the direct light from "pure" neon (Pl. I N⁰. 1, 2, 3, 4*a*) we notice a number of lines, which seem to form doublets, and a closer inspection shows that the following four doublets:

3163.6	3104.5	2906.9	2841.6
3149.6	3090.5	2895.2	2830.2

give a frequency difference between the components which is constant within the limit of error and equal to 142 cm^{-1}.

These doublets do not form any simple series, and only three of the lines are seen to be interpreted as belonging to series previously known. The component 2895.2 should be equal to ε (9.5), but particular interest is attached to the fact that for the first doublet one of the components 3163.6 belongs to the *D*- (or *d*-) series, while the second 3149.6 is a component of the multiple η-series.

These doublets can hardly be accidental, and if real they may be explained as being due to vibrations of molecular elements. If so, this would mean that the *D*- and η-series only differ with regard to the molecular quantum number. In other words the *D*-lines should be components of the multiple η-series.

Our thanks are due to Professor W. J. DE HAAS for his kindness in lending us the big quartz spectrograph. We also wish to express our sincere thanks to Cand. Real. LEIV HARANG for his very able assistance in connection with the experimental part of this work, and to Mr. S. STENSHOLT and Mr. S. VEDØ for most valuable assistance in connection with the treatment of observational material. We are also greatly indebted to a number of persons belonging to the scientific staff of the Cryogenic Laboratory at Leiden, and especially to Mr. G. J. FLIM, who is in charge of the installation for the production of liquid helium.

Physics. — *Measurement of the thermo-electric force per degree of some pure metals down to the temperature of liquid hydrogen, and calculation of the* THOMSON*-effect.* By G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON and J. O. LINDE. (Communication N⁰. 206*a* from the Physical Laboratory at Leiden.)

(Communicated at the meeting of January 25, 1930).

§ 1. *Introduction.* In a previous investigation BORELIUS, KEESOM and JOHANSSON [1] have measured the thermo-electric THOMSON-effect of two metal wires down to the temperature of liquid hydrogen. These wires were intended for, and have now been used as normals for indirect determinations of the THOMSON-effect (σ). Provided the THOMSON-equations be correct, the THOMSON-effect of any wire may be calculated from

$$\sigma = \sigma_{\text{norm.}} + T \cdot \frac{de}{dT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where e is its thermo-electric force per degree against the normal wire with a known THOMSON-effect ($\sigma_{\text{norm.}}$) and T is the temperature on the KELVIN-scale. The measurements of thermo-electric force dealt with in this communication embrace a number of pure metals. In a following paper data will be given concerning measurements on some systems of alloys.

§ 2. *Measuring method and apparatus.* The method used was indicated by BORELIUS [2] in conjunction with a theoretical investigation concerning the errors which may arise during ordinary determinations of the total thermo-electric force between a stable and a variable temperature, on account of inhomogeneities. Such inhomogeneities are found even in pure metals as a result of working or recrystallisation effects and are practically speaking unavoidable. For large temperature differences between the junctions, this may cause considerable errors, which are all the more dangerous as there is no possibility of correcting for them. For the measurements carried out now all the three junctions of a thermo-couple with its leads (Fig. 1) are brought to the temperature at which the measurement should be performed. By means of a heating coil the temperature of the middle junction is then

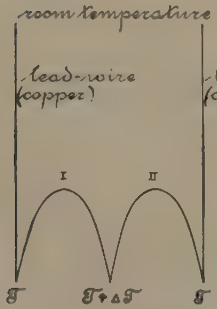

Fig. 1.

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[1] These Proceedings **31**, 1046, 1928. Comm. Leiden N⁰. 196*a*.

[2] G. BORELIUS, Ann. d. Phys. (4) **66**, 73, 1921.

slightly increased, by $\triangle T$, whereby a thermo-electromotive force $\triangle E$, is obtained. For the slight increase in the temperature $\triangle T$, the influence exerted by inhomogeneities in the measuring wires I and II will be of no consequence. The thermo-electric forces which may still occur in the leads may easily be eliminated, inasmuch as $\triangle E$ is measured as the difference in thermo-electromotive force when $\triangle T = 0$, and when $\triangle T$ has a finite value. Thus, we obtain the thermo-electric force per degree at the mean temperature $T_m = T + \frac{1}{2} \triangle T$ from

$$e = \frac{\Delta E}{\Delta T} \quad \ldots\ldots\ldots\ldots \quad (2)$$

and the temperature derivative $\frac{de}{dT}$ required for the measurement of the THOMSON-effect may then be obtained from the e-T-diagram by one single graphical derivation. The accuracy hereby obtained will be considerably greater than that attained by the measurement of the total emf E which requires a double derivation.

The inner parts of the apparatus used are shown in Fig. 2. They

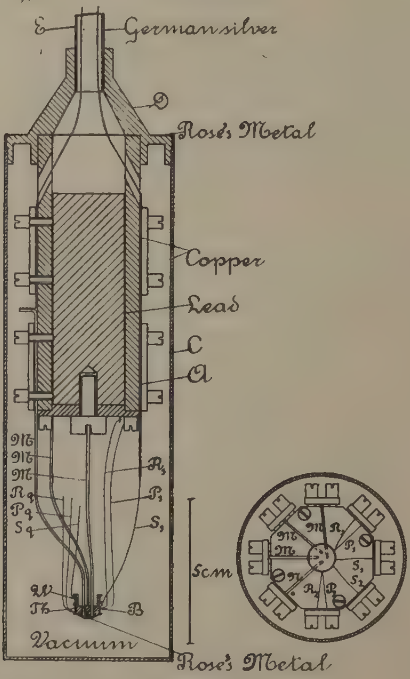

Fig. 2.

consisted of an octagonal copper tube A and a small copper piece B, between which the test wires M (length about 12 cm, diam. 0.75 to 1 mm) were fastened. The junctions must be electrically insulated but they should have a good thermal contact with the copper tube *A*. For that purpose on either side of these junctions, the test wires and the leads were carefully pressed against *A* for a distance of 3 to 4 cm and insulated only by means of cigarette paper. The opposite ends of the test wires were soldered with ROSE's metal directly to *B*. Besides the normal wire *N* three test wires *M* could be applied at the same time. By means of a heating coil *W*, the desired temperature-difference of *B* against *A* was obtained. *B* was further provided with a platinum thermometer *Th*, for measuring *T* and $\triangle T$. The whole was surrounded by the removable vacuum-tight copper covering C and was suspended by a long thin German silver tube *E* by means of which the arrangement was evacuated and the leads introduced. The apparatus thus closed, was surrounded by a hydrogen cryostat of the kind generally used in the Physical Laboratory at Leiden. In order to avoid disturbances as much as possible, all leads between the apparatus and the measuring table were covered by tubing, and the endpoints carefully guarded against radiation and air currents.

The apparatus was intended for carrying out measurements at constant as well as at varying temperatures. In the first case the cooling medium was introduced, so as to cover the apparatus completely, rising to 15 to 20 cm around the German silber tube. As no current passed through the heating coil *W* the entire apparatus, and thus also the thermometer *Th*, assumed the temperature of the surrounding cooling liquid. It could therefore be calibrated by means of a platinum thermometer, present in the cooling medium, the resistance-temperature curve of which was accurately known. In order to obtain a uniform temperature in the bath the cryostat was provided with a stirrer.

Measurements were generally carried out with the cooling liquid under two or three different pressures both in the case of liquid hydrogen and of liquid air. Further for each value of *T*, two different values for the temperature increase $\triangle T$, which with few exceptions ranged within a limit of 5—15 degrees were used. At the highest hydrogen temperature, determinations were however made with $\triangle T$ up to about 50 degrees, in order to obtain values within the range between liquid hydrogen and air.

After measurements at a constant temperature had been made the cooling liquid was removed from the cryostat by blowing. When the rate of rise of temperature became constant the temperature of *B* and the thermoelectric force arising on account of the temperature difference between *A* and *B* were determined, the current of the heating coil *W* being alternately switched on and off. From these measurements the temperature increase $\triangle T$ and the corresponding $\triangle E$ at a given mean temperature T_m could then be interpolated. In order to secure the greatest possible heat capacity at the lowest temperatures, and thus a slow rate of rise in temperature, the copper tube *A* was filled with a block of lead. Nevertheless, it proved difficult even in this way to obtain any good values within the range between liquid hydrogen and liquid air. At a higher temperature the rise in temperature was however slow and steady enough to make suitable measurements, and the values which were determined in this way starting from the temperature of hydrogen agree very well with the values obtained at a constant temperature within the temperature range of liquid air.

The resistance of the platinum thermometers was measured by means of a Thomson-bridge. A compensation apparatus according to Diesselhorst-Wolff and a Weston normal element were used for the measurements of the thermo-electromotive forces. The measurements were carried out simultaneously by two observers, and the final result e was obtained by dividing the values of $\triangle E$ and $\triangle T$ calculated from the respective readings independently of each other.

§ 3. *Renewed control of the earlier measurements of the* Thomson-*effect.* In the above mentioned work by Borelius, Keesom and Johansson 1) the Thomson-effect of one silver, and one copper wire, both alloyed with some gold, was measured. These alloys will now be called the silveralloy and the copperalloy. A control of the Thomson-effect was afforded by determining the total thermo-electromotive force of the element copperalloy-silveralloy between 0° C. and a few temperatures within the ranges of liquid hydrogen, liquid air, and room temperature. In this way values were calculated for the thermo-electric force per degree at 17.3° K., 70.6° K. and 280.7° K., and placed in the equation

$$e'' - e' = \int_{T'}^{T''} \left(\frac{\sigma_1}{T} - \frac{\sigma_2}{T} \right) dT, \quad \ldots \ldots \quad (3)$$

whereas the right-hand member was obtained by integrating $\frac{\sigma}{T}$ as function of the temperature. The deviations from equation (3) were found not to exceed the limits of accidental errors in the measurements of the thermo-electromotive forces.

We have now been able to make a more accurate control by measuring e with greater precision and at a considerably greater number of temperatures. The results will be found in the first column of Table I, and Fig. 3 shows the thermo-electric force per degree for the copperalloy and for copper against the silveralloy. The continuous curves have been traced through the points obtained by measurement, and the broken curves have been calculated from the earlier determinations of σ for the different wires, for which purpose the calculated values have been assumed to coincide with the observed ones at —150° C. At this temperature the accuracy of the σ-determinations may be assumed to be the greatest, inasmuch as the influence of radiation is slight and at the same time the heat conductivity is nearly

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1) G. Borelius, W. H. Keesom and C. H. Johansson, loc. cit.

independent of the temperature[1]). The difference between observed and calculated e-values is probably greater than the experimental errors in the

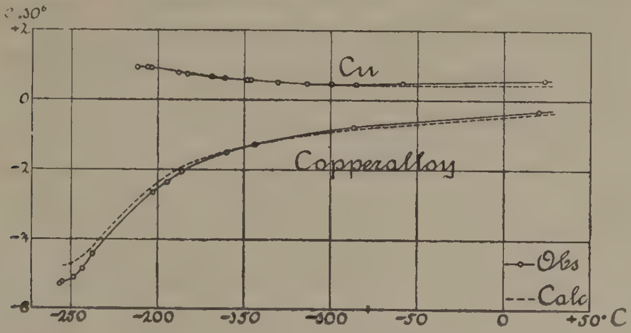

Fig. 3.
Volt per degree against silveralloy.

TABLE I.
Thermo-electric Force in Microvolt per degree.

Copperalloy normal 1 against silveralloy normal		Copperalloy normal 2 against copperalloy normal 1		Copperalloy (not enamelled) against copperalloy normal 1	
t_m °C	e	t_m °C	e	t_m °C	e
—256.5	—5.30	—256.7	+0.01	—256.5	—0.737
255.0	5.23	254.0	±0.00	255.0	0.703
248.6	5.11	251.4	—0.01	248.6	0.528
243.4	4.85	205.4	+0.04	243.4	0.712
237.5	4.43	204.6	0.04	237.5	0.677
202.8	2.66	197.2	0.01	202.8	0.497
194.5	2.37	192.5	0.02	194.5	0.465
186.0	2.06	188.1	0.03	186.0	0.439
160.2	1.51	179.2	0.05	157.6	0.33
143.8	1.28	169.8	—0.02	140.9	0.29
86.4	0.79	144.6	+0.04	85.2	0.21
+20.2	0.323	116.1	0.05	+20.2	0.145
		85.1	0.07		
		+3.36	0.07		

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[1]) Cp. the cited paper.

new measurements of thermo-electric force, and may probably be referred to the uncertainty of the determinations of the THOMSON-effect. On account of the absolute values of the THOMSON-effect of the silveralloy being considerably lower than those of the copperalloy the absolute accuracy of the silveralloy will be greater than that of the copperalloy. For the calculation of the THOMSON-effects from the measurements carried out now according to equation (1) we have therefore considered the directly measured values of the THOMSON-effect of the silveralloy to be correct. All the measurements of thermo-electric force have therefore been made against the silveralloy as the normal wire. Accordingly we used exactly the same piece of wire for which σ had been directly determined. Also the copperalloy 1 in Table I consists of a piece of the alloyed copper wire which was previously used for determining σ. In order to ascertain to what extent the thermo-electric force varied from one part to another of the same kind of wire, measurements were carried out on another arbitrarily chosen piece of the same enamelled copperalloy wire against the copperalloy 1. The result will be found in the middle column of Table I. It is evident from this that even if the difference exceeds the experimental error, it must still be considered to be small, amounting at the utmost to 0.07 microvolt per degree. Further we measured the thermo-electric force of a copperalloy wire, produced at the same time as copperalloy 1, but not enamelled. As may be seen from column 3 in Table I, the thermo-electric force per degree is considerably greater in this case, and the measurement shows that the slight increase in temperature to which the hard-drawn wire was subjected during the enamelling (300° C. during 2 min.) has proved sufficient to alter the thermo-electric properties perceptibly.

§ 4. *Starting material and the production of test-wires.* As starting material was used :

Cu technically pure with selected low resistivity.
Ag "Kahlbaum" pro analysi.
Au pure from Heraeus.
Fe very pure ; electrolytic, vacuummolten, from Heraeus.
Pd extra pure from Heraeus.
Pt very pure from Heraeus.
Pb very pure.

The metals were used in the form of wires of 1 mm diameter, which had been annealed after drawing.

§ 5. *Thermo-electric force and* THOMSON-*effect of pure metals.* For this investigation we have measured the thermo-electric force per degree for the metals *Cu, Ag, Au, Fe, Pd, Pt* and *Pb*, all with cubic structure, against the silveralloy, between —256 and +20° C. The results are collected in table II, and in Figs. 4—6 the e, T-curves so obtained are represented. By graphical differentiation of these curves using temperature intervals of 20 degrees we have calculated the THOMSON-coefficients of the different

TABLE II. Thermoelectric Force in Microvolt per degree against silveralloy.

Cu I		*Cu II*		*Ag*		*Au*		*Fe*		*Pt*		*Pd*	
t_m °C	e	t_m °C	e	t_m °C	e	t_m °C	e	t_m °C	e	t_m °C	e	t_m °C	e
−256.7	+0.051	−188.0	+0.792	−256.4	−0.264	−256.4	−1.45	−256.7	+0.027	−256.5	+1.28	−258.3	+0.505
254.3	0.067	182.9	0.738	254.2	0.057	254.2	0.962	254.3	0.097	255.0	1.55	252.8	0.805
251.6	0.100	161.1	0.62	251.5	+0.034	251.5	0.785	251.8	0.218	248.6	2.49	246.4	1.485
249.6	0.144	148.2	0.56	248.6	0.177	248.6	0.471	251.6	0.206	243.4	3.11	239.9	2.15
245.2	0.291	130.7	0.495	241.7	0.357	241.7	0.101	249.6	0.330	237.5	3.86	228.6	2.83
240.0	0.452	113.9	0.46	235.2	0.377	235.2	+0.044	245.2	0.743	202.8	5.38	200.8	3.51
214.1	0.922	99.5	0.455	213.8	0.378	215.3	0.275	240.0	1.375	194.5	5.24	193.2	3.15
206.0	0.925	85.2	0.445	195.4	0.316	196.3	0.300	214.1	5.95	186.0	4.75	185.4	2.56
203.7	0.913	+23.65	0.572	180.0	0.250	181.2	0.295	206.0	7.47	157.6	2.84	170.3	1.385
188.2	0.787			163.3	0.230	164.9	0.330	203.7	7.80	140.9	1.71	151.8	−0.105
188.0	0.788			148.8	0.219	149.5	0.357	189.8	10.10	85.2	−1.47	95.4	4.25
168.7	0.667			66.1	0.197	66.5	0.494	188.0	10.25	+20.2	6.54	75.6	5.50
147.2	0.561			+22.2	0.232	+22.2	0.657	169.4	12.84			+15.3	11.28
58.5	0.472							147.9	15.2				
+24.02	0.558							59.1	17.2				
								+24.02	15.15				

metals in accordance with equation (1). The values obtained have been used to draw the σ, T-curves that are found in Figs. 7—10. Finally the

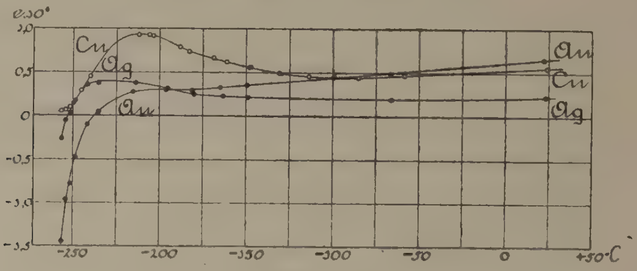

Fig. 4.
Volt per degree for *Cu I* and *II*, *Ag*, and *Au*, against silveralloy.

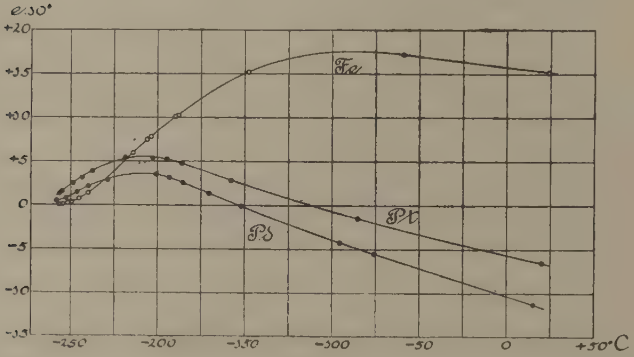

Fig. 5.
Volt per degree for *Pt*, *Pd* and *Fe* against silveralloy.

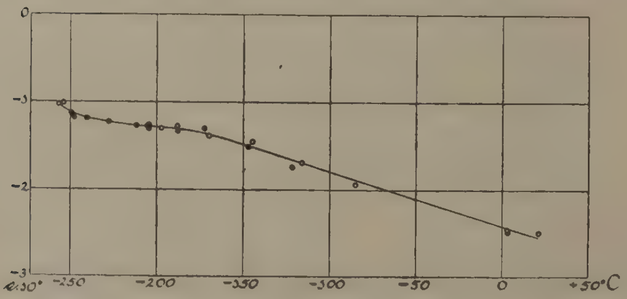

Fig. 6.
Volt per degree for *Pb* against silveralloy.

THOMSON-coefficients of the respective metals have been read off on the σ, T-curves for every ten degrees between 20 and 180° K. and for every 20 degrees between 200 and 300° K., and the values are given in table III. In this table we have moreover included the THOMSON-coefficients of the cubically crystallising metals *Ni* and *Co* (Fig. 9) calculated from

WIETZEL's ¹) thermo-electric measurements against lead, and also those for both the axial directions of the hexagonally crystallising metals *Zn* and

TABLE III. THOMSON-effect in Microvolt per degree.

T	*Cu*	*Ag*	*Au*	*Pd*	*Pt*	*Fe*	*Ni*	*Co*	*Pb*
20	+0.59	+1.40	+2.83	+1.9	+3.2	+1.3	—	—	—
25	1.04	1.23	2.09	2.6	3.6	2.7	—	—	—
30	1.22	0.85	1.58	3.1	3.9	4.1	—4.5	—0.2	0.00
40	1.03	0.24	0.88	3.2	3.8	6.7	5.4	0.3	—0.04
50	0.67	—0.02	0.45	2.5	2.7	9.0	5.0	0.8	0.06
60	0.18	0.17	0.19	1.0	1.0	10.8	4.5	2.0	0.09
70	—0.29	0.24	0.07	—1.5	—1.1	11.9	4.1	3.7	0.12
80	0.46	0.25	0.05	4.6	3.3	12.6	4.0	5.5	0.15
90	0.48	0.17	0.17	6.6	5.1	12.9	4.0	7.0	0.18
100	0.45	0.03	0.32	7.8	6.5	13.0	4.5	8.4	0.20
110	0.37	+0.12	0.45	8.7	7.5	13.0	5.3	9.8	0.23
120	0.26	0.25	0.56	9.3	8.0	12.8	6.4	11.1	0.26
130	0.13	0.35	0.66	9.7	8.2	12.2	7.4	12.4	0.29
140	+0.02	0.44	0.75	10.1	8.2	11.0	8.3	13.5	0.32
150	0.17	0.52	0.83	10.3	8.3	8.9	9.0	14.6	0.34
160	0.31	0.59	0.91	10.6	8.4	6.1	9.7	15.7	0.37
170	0.46	0.66	0.99	10.9	8.5	2.6	10.3	16.7	0.40
180	0.59	0.72	1.06	11.2	8.7	—0.2	10.9	17.6	0.42
200	0.79	0.84	1.19	12.1	9.1	3.5	12.1	19.6	0.46
220	0.96	0.96	1.31	13.3	9.8	4.5	13.3	21.5	0.49
240	1.10	1.08	1.43	14.6	10.6	4.8	14.5	23.4	0.52
260	1.24	1.20	1.54	15.8	11.4	5.2	15.7	25.4	0.54
280	1.38	1.32	1.66	17.0	12.3	5.6	—	—	0.55
300	1.52	1.44	1.77	18.2	13.2	5.9	—	—	0.57

Cd (Figs. 11 and 12), calculated from the thermo-electric measurements of GRÜNEISEN and GOENS ²) with single-crystals against *Cu*. Evidently the

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¹) G. WIETZEL, Ann. d. Phys. **43**, 605, 1914.

²) E. GRÜNEISEN und E. GOENS, Zs. f. Phys. **37**, 278, 1926.

possibility of calculating the THOMSON-coefficients in this manner from earlier measurements of thermo-electric forces, depends on the agreement between the THOMSON-coefficients of the reference metals there employed, viz. *Pb* and *Cu*, and those used by us. However, we have reason to assume that the errors caused by a difference of this kind are small. Thus the THOMSON-coefficient for *Pb* is small over the whole temperature-range, compared with those of *Ni* and *Co*, so that proportionally great deviations in the values of the two *Pb*-species are needed to give considerable absolute errors in the values for *Ni* and *Co*. As to the THOMSON-coefficient for *Cu* we are able to estimate the difference between species of different origin, by comparing our values of the thermo-electric force per degree against *Pb* with the values obtained by WIETZEL as well as by KRUPKOWSKI and DE HAAS [1]) for the same combination. The deviations between the different measurements which in the temperature-range —50 to —230° C. amount to some tenths of a microvolt per degree, consist principally in a parallel displacement of the *e*, *T*-curves along the *e*-axis. The agreement is therefore satisfactory.

It is evident from Fig. 7, that the temperature function of the THOMSON-effect in the three metals belonging to the coppergroup is very similar. At high temperatures the metals *Cu*, *Ag* and *Au* give positive values which decrease with the temperature to a minimum, situated for *Cu* at 88° K., and for *Ag* and *Au* at 76° K. At still lower temperatures *Cu* has a maximum at about 30° K. *Ag* shows a certain tendency towards such a maximum, which would then be situated below 20° K., whilst *Au* only shows a rise without any tendency whatever towards a maximum at the lowest temperatures reached here. Measurements of thermo-electromotive force by KAMERLINGH

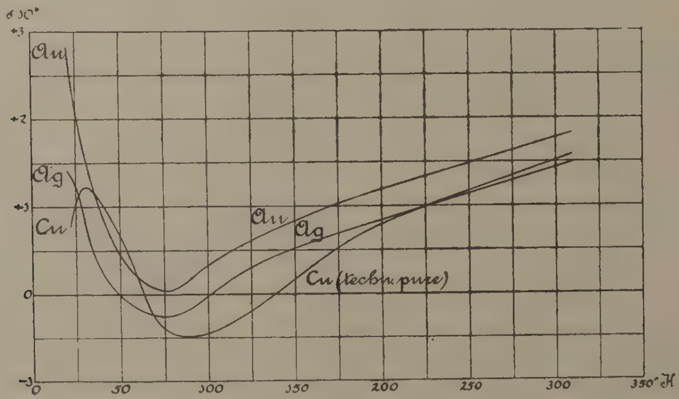

Fig. 7.
THOMSON-effect for *Cu*, *Ag* and *Au*.

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[1]) A. KRUPKOWSKI and W. J. DE HAAS, These Proc. 32, 921, 1929. Comm. Leiden N⁰. 194*b*.

ONNES and HOLST [1]) carried out on various kinds of gold, confirm the view that the rise observed is characteristic of gold, though the course of the curve varies considerably in different wires. However, at still lower temperatures they found a decreasing thermo-electric force per degree, corresponding to the formation of a maximum in the σ-curve. Consequently, this maximum is certainly present even here, though displaced to very low temperatures. The displacement of the maxima and minima towards lower temperatures proceeding from copper to silver and gold, may possibly stand in a certain relation to the characteristic temperatures of the metals [2]), these being about 320° for *Cu*, 220° for *Ag* and 190° for *Au*. The accordance with WIETZEL's [3]) measurements is good for all these metals.

In the platinumgroup also the temperature function of the THOMSON-effect (Fig. 8) is very similar for the two metals investigated. At high temperatures *Pd* and *Pt* give negative values approximately proportional to the absolute temperature. At about 70° K. the curves intersect the zero axis, then giving a maximum on the positive side at 37° K. for *Pd* and 34° K. for *Pt*. This is in accordance with the fact that the characteristic temperature is in the case of *Pd* somewhat higher than in the case of *Pt*.

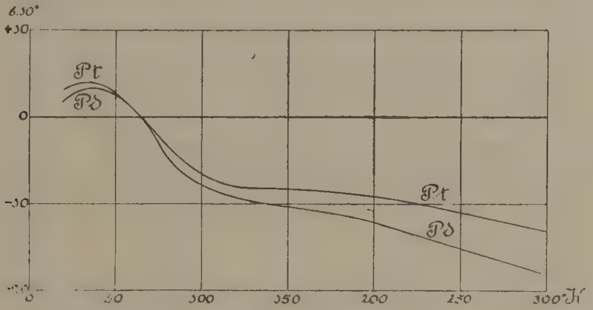

Fig. 8.
THOMSON-effect for *Pt* and *Pd*.

The σ-curve for *Fe* (Fig. 9) shows a great analogy with that of the platinum metals. Thus, it is negative at high temperatures, and at a lower temperature it intersects the zero axis, having a maximum on the positive side, here situated at about 100° K. In this case the *e*, *T*-curve against *Pb*, which has a very characteristic course, proceeds similarly when derived either from WIETZEL's or from our measurements, only somewhat displaced in the direction of the e-axis, which may probably be referred to a different starting material.

The σ-curves for *Ni* and *Co* calculated from WIETZEL's measurements of thermo-electric forces do not show a great similarity either mutually or compared with the curve for *Fe*. However, it must be pointed out that it is

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[1]) H. KAMERLINGH ONNES and G. HOLST, These Proc. **17**, 760, 1917. Comm. Leiden N⁰. 142c.

[2]) G. BORELIUS und F. GUNNESON Ann. d. Phys (4) **65**, 520, 1921. E. GRÜNEISEN und E. GOENS, loc. cit.

[3]) G. WIETZEL, loc. cit.

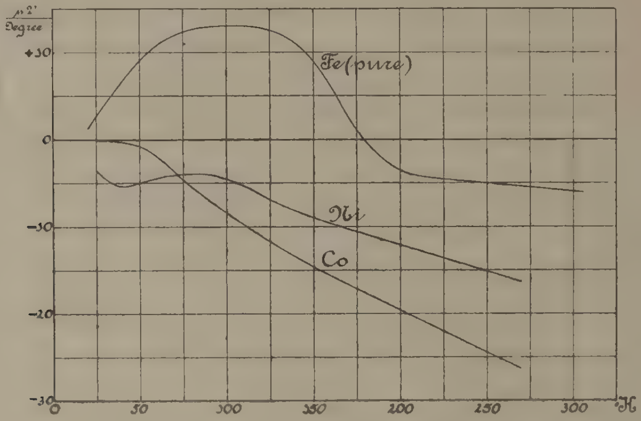

Fig. 9.
THOMSON-effect for *Fe*, *Ni* and *Co* (*Ni* and *Co* calculated from WIETZEL's measurements of the thermo-electromotive force).

very difficult to get the metal pure especially with *Co*. Nevertheless these curves have been included because the metals *Co* and *Ni* were used in some of the *Cu*-alloys investigated by us [1]), and also they are the only existing measurements on these metals.

The measurements of thermo-electric force carried out for lead were made before the apparatus had been finally tested and the uncertainty is therefore much greater here than in other measurements. In order to trace the THOMSON heat curve (Fig. 10) consideration was therefore taken of BORELIUS' and GUNNESON's [2]) measurements of σ. At 120, 150 and 200° K.

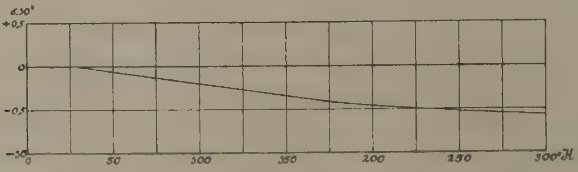

Fig. 10.
THOMSON-effect for *Pb*.

their values tally well with those now obtained, but at 300° K. they are somewhat more negative. Within the entire temperature interval investigated the THOMSON-effect is small and negative and approaches to the zero axis on decreasing the temperature.

For *Zn* and *Cd* GRÜNEISEN and GOENS have given the differences between the THOMSON-coefficients measured perpendicularly to and parallel with the hexagonal axis of *Zn* and of *Cd* from about 20 to 270° K. From their measurements against *Cu* we have now been able to determine the σ-curves for the different crystal directions separately. (*Zn* Fig. 11, *Cd* Fig. 12).

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[1]) Cf. the following paper, Comm. Leiden N⁰. 206*b*.

[2]) G. BORELIUS und F. GUNNESON, loc. cit.

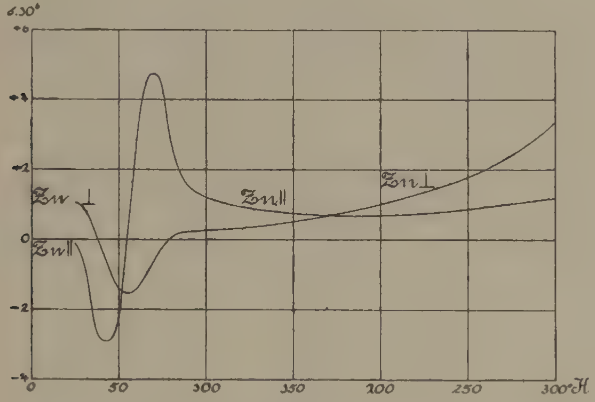

Fig. 11.

THOMSON-effect for *Zn*-crystal (calculated from GRÜNEISEN and GOENS' measurements of the thermo-electromotive force).

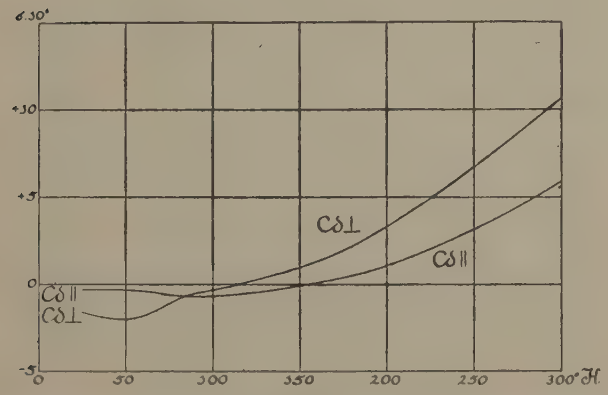

Fig. 12.

THOMSON-effect for *Cd*-crystal (calculated from GRÜNEISEN and GOENS' measurements of the thermo-electromotive force).

For *Zn* the curves so obtained referring to the different axial directions, are as complicated as those showing the difference between the THOMSON-effects 1). For *Cd* the latter has a rather more irregular course. Yet there is some confirmation of an assumption of GRÜNEISEN and

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1) GRÜNEISEN und GOENS, loc. cit. fig. 8.

Goens that influences on the thermo-electric force caused by atomic dissimilarities are eliminated for such a difference. Thus the course of the $\sigma_{\text{diff.}}, T$-curves is upon the whole similar for both the metals with the maxima and minima of the *Zn*-curve displaced towards lower temperatures compared with those of the *Cd*-curve, which possibly may be connected with the fact that the mean value of the characteristic temperature of *Zn* is at about 230° K. and of *Cd* at about 156° K., as Grüneisen and Goens have already remarked. Such a correspondence between the two metals can hardly be traced from the σ-curves for a single axisdirection.

§ 6. *Thermo-electric force per degree for pure metals at corresponding temperatures.* In order to facilitate the calculation for a given temperature of the thermo-electric force per degree of an arbitrarily chosen combination of the metals investigated, this magnitude, measured against the silveralloy, is given in Table IV for every 20 degrees. The values are obtained from curves, drawn through the directly determined points.

TABLE IV. Thermoelectric Force in Microvolt per degree against silveralloy.

t °C	*Cu*	*Ag*	*Au*	*Pd*	*Pt*	*Fe*	*Pb*
−255	+0.07	−0.10	−1.20	+0.75	+1.54	+0.05	−1.06
240	0.45	+0.37	0.05	2.10	3.60	1.40	1.19
220	0.90	0.39	+0.24	3.40	5.24	4.80	1.25
200	0.89	0.31	0.30	3.48	5.40	8.45	1.29
180	0.72	0.25	0.30	2.14	4.36	11.5	1.33
160	0.61	0.22	0.33	0.54	3.02	14.0	1.42
140	0.52	0.21	0.37	−1.06	1.72	15.8	1.54
120	0.47	0.20	0.40	2.52	0.50	16.9	1.67
100	0.44	0.20	0.44	3.92	−0.70	17.5	1.79
80	0.45	0.20	0.47	5.27	1.76	17.5	1.92
60	0.47	0.20	0.51	6.52	2.80	17.3	2.05
40	0.49	0.20	0.55	7.80	3.80	16.9	2.17
20	0.51	0.20	0.58	9.05	4.72	16.2	2.29
±0	0.53	0.21	0.62	10.32	5.62	15.8	2.42
+20	0.56	0.22	0.65	11.6	6.56	15.3	2.54

§ 7. *Conclusion.* Inspection of the σ-curves (Figs. 7—12) as well as of the e-curves (Figs. 4—6) shows once more the desirability of making measurements at the temperatures obtainable which liquid helium. Only so can the validity of the limiting laws [1]) $\sigma \rightarrow 0$ and $e \rightarrow 0$ for $T \rightarrow 0$ be tested. In the meantime the experimental curves in general seem more or less to tend towards a verification of those laws, especially as regards the THOMSON-effect.

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[1]) W. H. KEESOM, These Proceedings **16**, 236, 1913. Comm. Leiden Suppl. N⁰. 30*b*. W. NERNST, Theoretische Chemie 1913, p. 753.

Physics. — *Measurement of the thermo-electric force per degree of some alloys down to the temperature of liquid hydrogen, and calculation of the* THOMSON*-effect.* By G. BORELIUS, W. H. KEESOM, C. H. JOHANSSON and J. O. LINDE. (Communication N⁰. 206*b* from the Physical Laboratory at Leiden).

(Communicated at the meeting of January 25, 1930).

§ 1. *Introduction.* Just as we did for some pure metals [1]) we also measured the thermo-electric force of a number of alloys down to the temperature of liquid hydrogen. For the method of measurement and the apparatus we refer to the former paper.

As a normal, against which the thermo-electric force was measured, we again chose the silveralloy wire (cf. § 3 of the former paper), the THOMSON-effect of which has been measured by BORELIUS, KEESOM and JOHANSSON [2]).

§ 2. *Starting material and the production of test-wires.* As starting material for the preparation of the alloys we used :

Cu "Kahlbaum" pro analysi, electrolytic,
Ni ,, ,, ,, free from cobalt,
Co ,, ,, ,,
Fe ,, ,, ,,
As pure from Kahlbaum,
Pd extra pure from Heraeus,
Au pure from Heraeus.

The platinumalloys (*PdRh* and *PtPdAu*) were obtained in the form of 1 mm wires, which had been annealed after drawing. They had been produced and placed at our disposal by Messrs W. C. HERAEUS in Hanau. The copperalloys had originally been produced for another investigation by one of the present authors (J. O. LINDE). They had been fused in vacuo and carefully homogenized near the melting point. After rolling and drawing to wires with a diameter of 0.75 mm, they had been annealed at 380° C.

§ 3. *Thermo-electric Force and* THOMSON*-effect in Alloys.* We investigated the following alloys : binary alloys of *Cu* with small quantities of *Fe, Co, Ni, Pd, As* and *Au*, binary alloys of *Pt*, containing 1.9—17.4 *At %*

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[1]) Cf. These Proceedings **33**, 17, 1930. Comm. Leiden N⁰. 206*a*.

[2]) These Proceedings **31**, 1046, 1928. Comm. Leiden N⁰. 196*a*.

TABLE I.

Thermo-electric Force in Microvolt per degree against silveralloy.

$Cu + 0.075$ *At* % *Fe*		$Cu + 0.17$ *At* % *Fe*		$Cu + 0.09$ *At* % *Co*	
t_m °C	*e*	t_m °C	*e*	t_m °C	*e*
−256.4	−15.65	−188.0	−9.57	−188.0	−7.37
254.2	15.85	182.9	9.10	182.9	7.38
251.5	16.25	160.3	8.5	158.5	8.3
248.6	16.4	147.3	8.05	146.2	8.65
241.7	15.2	129.9	7.4	128.0	8.85
235.2	14.5	113.7	6.95	112.9	9.1
215.3	11.3	98.9	6.8	98.1	9.55
196.3	10.0	84.6	6.45	84.2	9.65
181.2	8.5	+23.65	5.03	+23.65	10.94
164.9	7.8				
149.5	7.3				
66.5	5.05				
+22.2	3.87				

TABLE I (*continued 1*).

Thermo-electric Force in Microvolt per degree against silveralloy.

$Cu + 1.12$ *At* % *Ni*		$Cu + 2.16$ *At* % *Ni*		$Cu + 3.32$ *At* % *Ni*		$Cu + 3.32$ *At* % *Ni* heated at 700 °C	
t_m °C	*e*	t_m °C	*e*	t_m °C	*e*	t_m °C	*e*
−256.4	−1.92	−256.4	−1.8	−256.4	−1.81	−256.7	−1.54
253.8	2.05	253.8	2.00	253.8	1.97	254.3	1.80
239.0	2.55	239.0	2.88	239.0	2.74	251.7	2.10
232.2	2.87	229.3	3.58	229.3	3.32	249.6	2.21
229.3	2.85	229.2	3.62	228.2	3.41	245.2	2.48
212.2	3.29	211.1	4.56	209.8	4.21	240.0	2.81
203.7	3.54	203.7	4.97	203.7	4.48	210.0	4.56
199.8	3.59	199.8	5.08	199.8	4.57	206.0	4.88
193.4	3.84	192.2	5.30	191.6	4.84	203.7	4.98
188.0	3.90	188.0	5.63	188.0	5.04	188.0	5.74
176.5	4.17	176.5	5.50	176.5	6.03	187.4	5.81
164.9	4.68	164.9	5.98	164.9	6.77	167.3	6.87
148.7	4.83	145.0	6.62	145.0	7.48	146.7	8.04
129.4	5.27	129.4	7.18	129.4	8.19	58.1	12.50
114.3	6.05	114.3	7.91	114.3	9.22	+24.02	16.50
101.9	5.83	101.9	8.20	101.9	9.48		
+17.7	8.66	+17.7	15.06	+17.7	12.68		

TABLE I (*continued 2*).

Thermo-electric Force in Microvolt per degree against silveralloy.

$Cu + 0.51$ *At* % *As*		$Cu + 1.01$ *At* % *As*		$Cu + 1.35$ *At* % *As*	
t_m °C	*e*	t_m °C	*e*	t_m °C	*e*
−254.9	−0.387	−254.9	−0.326	−254.9	−0.333
251.8	0.396	251.8	0.360	251.8	0.361
247.7	0.418	247.7	0.398	247.7	0.413
243.2	0.391	243.2	0.415	243.2	0.444
232.6	0.381	232.6	0.464	232.6	0.500
206.5	0.427	206.5	0.583	206.5	0.649
203.8	0.439	203.8	0.589	203.8	0.640
195.8	0.502	195.8	0.653	195.8	0.700
187.7	0.582	187.7	0.728	187.7	0.778
174.2	0.693	174.0	0.816	173.4	0.866
152.5	0.843	151.6	0.941	151.1	0.984
63.2	1.528	62.6	1.613	62.0	1.671
+15.6	2.135	+15.6	2.30	+15.6	2.39

TABLE I (*continued 3*).

Thermo-electric Force in Microvolt per degree against silveralloy.

$Cu + 1.01$ *At* % *Pd*		$Cu + 1.99$ *At* % *Pd*		$Cu + 3.01$ *At* % *Pd*	
t_m °C	*e*	t_m °C	*e*	t_m °C	*e*
−204.5	−1.01	−204.5	−1.38	−204.5	−1.44
199.3	1.015	199.3	1.40	199.3	1.47
188.3	1.01	188.3	1.42	188.3	1.52
183.8	1.00	183.8	1.41	183.8	1.52
168.0	1.03	166.6	1.46	166.3	1.65
149.4	1.02	149.0	1.51	147.7	1.71
78.9	1.06	78.2	1.68	77.7	2.02
60.7	1.09	60.0	1.74	59.2	2.13
+22.74	1.18	+22.74	2.02	+ 22.74	2.64

TABLE II.

Thermo-electric Force in Microvolt per degree against silveralloy.

Pt + 1.9 *At* % *Rh*		*Pt* + 3.5 *At* % *Rh*		*Pt* + 9.1 *At* % *Rh*		*Pt* + 17.4 *At* % *Rh*		*Pt Pd Au*-alloy	
t_m °C	e	t_m °C	e	t_m °C	e	t_m °C	e	t_m °C	e
—252.5	+1.42	—252.5	+1.29	—252.5	+0.96	—258.3	+0.484	—258.3	—2.81
249.9	1.72	249.9	1.52	249.9	1.13	252.8	0.670	252.8	3.35
245.8	2.12	245.8	1.83	245.8	1.34	246.4	0.961	246.4	4.30
240.6	2.69	240.6	2.34	240.6	1.69	239.9	1.19	239.9	5.18
230.8	3.28	230.8	2.86	230.8	2.06	228.6	1.44	228.6	6.42
203.5	4.23	203.5	3.77	203.5	2.79	200.8	1.84	200.8	9.92
198.0	4.10	198.0	3.69	198.0	2.76	193.2	1.84	193.2	10.60
182.7	3.70	182.7	3.42	182.7	2.67	185.4	1.80	185.4	11.28
164.0	3.14	162.3	2.99	163.3	2.52	169.1	1.71	167.5	13.0
143.3	2.24	141.3	2.29	142.6	2.17	150.5	1.66	149.7	15.2
121.3	1.44	119.7	1.71	120.5	1.86	93.4	1.09	94.2	21.4
100.3	0.49	99.4	0.94	99.8	1.41	75.0	0.87	74.1	23.0
+26.17	—4.25	+26.17	—3.06	+26.17	—1.17	+15.3	0.291	+15.3	33.7

Rh and also a physically-technically interesting ternary *Pt, Pd, Au*-alloy.

The binary alloys chosen represent two different types. Like most dilute alloys, all the copperalloys are thermo-electrically negative against the pure metal, whilst the *PtRh*-alloys range amongst those alloys of the platinum group of metals which (at ordinary temperatures) are thermo-electrically positive against the pure metals. The results of the measurements of thermo-electric force per degree against the silveralloy normal are given in Tables I and II. In Figs. 1—6 are plotted the thermo-electric force per degree of the alloys against the pure metal in question (*Cu, Pt*).

The copper alloys with small quantities of iron are especially interesting inasmuch as their thermo-electric force per degree against pure copper rises with decreasing temperature (Fig. 1). Thus, *Cu* with 0.075 *At* % *Fe* (against *Cu*) at —255° C attains a value many times exceeding the values which have previously been obtained with any investigated combination at this low temperature. Even at room temperature the thermo-electric force per degree, calculated per atomic per cent admixture, is abnormally high, with a value of 4.46 Volt/degree (against copper) at + 20° C and 0.075 *At* % *Fe*. A still greater influence is exerted at this temperature by an admixture of Co, giving 11.51 Volt/degree (against copper) at + 20° C and 0.09 *At %* *Co*. In this case, however, the thermo-electric force per degree decreases with the temperature. The solubility of *Fe* as well as *Co*

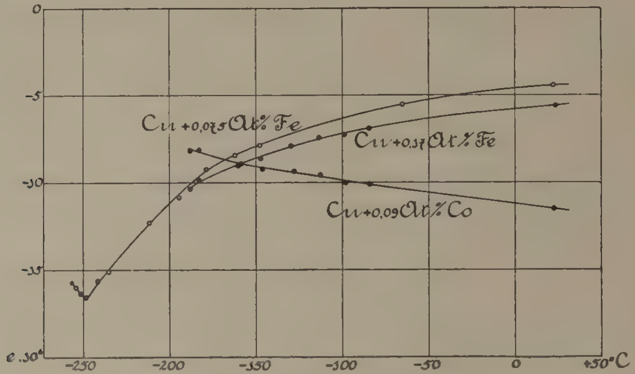

Fig. 1. Volt per degree against *Cu*.

in copper is small, so that the alloys in question approach the saturation limit. Indeed the alloy with 0.17 *At % Fe*, at the annealing temperature applied, surpasses this limit, and holds a phase rich in iron embedded in the phase of copper saturated with iron. It rendered values of the thermo-electric force only slightly higher than *Cu* with 0.075 *At % Fe*.

Alloys of *Cu* with *Ni* — of which those containing about 1, 2 and 3 *At % Ni* were investigated — render thermo-electric forces, decreasing with the temperature (Fig. 2). This system is completely miscible in the solid condition. Measurements of KRUPKOWSKI [1]) on rods of a *CuNi*

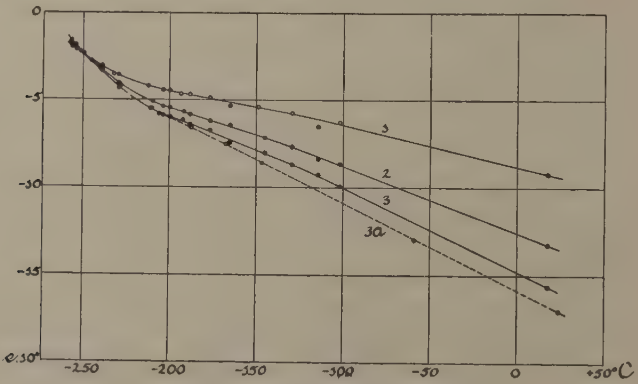

Fig. 2 *Cu Ni*-alloys against *Cu*.

1. *Cu* + 1.12 *At* % *Ni*, heated at 380° C.
2. „ „ 2.16 „ „ „ „ „ „ „
3. „ „ 3.32 „ „ „ „ „ „ „
3a. „ „ „ „ „ „ „ „ 700° C.

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[1]) A. KRUPKOWSKI, Revue de Métallurgie Nr. 3 and 4, 1929.

alloy with 2.3 *At % Ni* agree well with our measurements of an alloy with 2.2 *At % Ni* at 0° and —39° C., while between those of KRUPKOWSKI and DE HAAS [1]) on wires of such an alloy at —91.52, —193.96 and —228.71° C. and our results there are deviations.

Concerning the curves for the THOMSON-effect for the dilute alloys of *Cu* with *Fe* and *Ni* respectively (Fig. 7) it is worth mentioning that the addition of small quantities of *Fe* to *Cu* gives positive THOMSON-effects with a curve-shape that recalls the THOMSON-effect curve for the pure iron (Fig. 9 of the former paper) whilst the addition of small quantities of *Ni* gives negative THOMSON-effects with a shape of the curve that recalls that of the pure *Ni* (Fig. 9 of the former paper).

An addition of *As* to *Cu* renders against pure copper fairly small thermo-electric forces. In considering the influence of concentration it strikes one, that an increase in the admixture from 0.51 to 1.01 and 1.35 *At % As* gives only a relatively slight increase in the thermo-electric force. In this system the saturation limit is situated above 1.35 *At % As* at the annealing temperature 380° C. The measurements of these alloys just like those of the copper-nickel alloys show that below —250° C the most dilute one gives the greatest thermo-electric force against the pure metal.

The *Cu Pd*-alloys with about 1, 2 and 3 *At % Pd* (Fig. 3) have only been investigated down to —205° C. They render medium thermo-electric forces, within the investigated interval, varying but slightly with the temperature. The system shows complete miscibility in the solid condition.

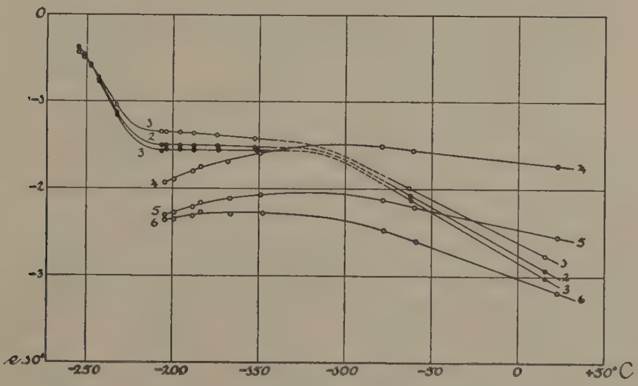

Fig. 3. Volt per degree $Cu + As$ and $Cu + Pd$ against Cu.

1. $Cu + 0.51$ *At* % *As*	4. $Cu + 1.01$ *At* % *Pd*
2. „ „ 1.01 „ „ „	5. „ „ 1.99 „ „ „
3. „ „ 1.35 „ „ „	6. „ „ 3.01 „ „ „

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[1]) A. KRUPKOWSKI and W. J. DE HAAS. These Proceedings 32, 921, 1929. Comm. Leiden N⁰. 194*b*.

The dilute alloys of *Cu* with *Au* were investigated specially extensively because the *Cu*-alloy with 0.37 *At %* *Au*, used as normal, had given a strikingly great thermo-electric force against pure *Cu* at the low temperatures. However, as may be seen from Fig. 4, the six investigated alloys, all produced with *Cu* from KAHLBAUM and the very purest *Au* from HERAEUS show no regularity in the influence exerted upon the thermo-electric force by the concentration. It is evident that these irregularities have been caused by some impurity or some mechanical working, the influence of which at these low temperatures is stronger than that of the added gold. It is to be observed that from the results for the system *CuFe* there is good reason to assume that extremely small impurities of iron, perhaps even some few thousandths per cent are enough to produce the variations in the thermo-electric force observed with the *CuAu*-alloys. We have given Fig. 4 only to emphasize the difficulties of getting reproduceable values for certain systems of dilute alloys.

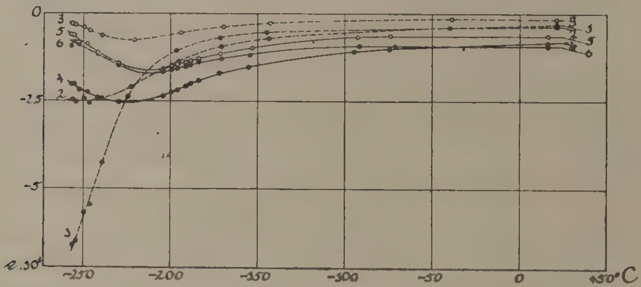

Fig. 4. *Cu Au* alloys against *Cu*.

1. *Cu* + 0.05 *At* % *Au*
2. „ „ 0.10 „ „ „
3. „ „ 0.20 „ „ „
4. *Cu* + 1.0 *At* % *Au*
5. „ „ 2.0 „ „ „
6. „ „ 3.0 „ „ „

As already mentioned, the alloys of *Pt* and *Rh* at high temperatures render positive thermo-electric forces against *Pt*. At low temperatures, however, even here (see Fig. 5) negative thermo-electric forces are obtained

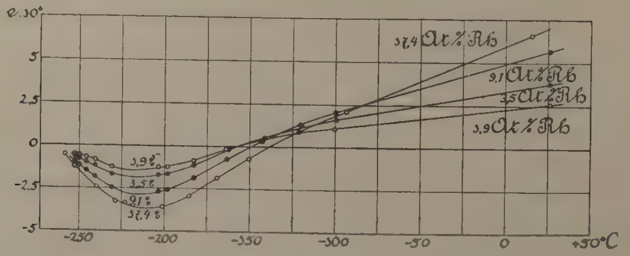

Fig. 5. Volt per degree for *PtRh*-alloys against *Pt*.

against the primary metal. A very clear view of the state at different temperatures is obtained if isotherms are drawn in the concentration diagram (Fig. 6). As will be seen there, these alloys change at about —150° C from giving positive thermo-electric forces to giving negative ones. The curves at room temperature and at —250° C are approximately mirror images of each other in this diagram.

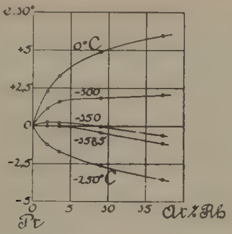

Fig. 6. Volt per degree for *PtRh*-alloys against *Pt*

Values of the THOMSON-effect have been calculated for the systems *CuNi*, *CuAs*, *CuFe* and *PtRh*, and are given in Tables III and IV and

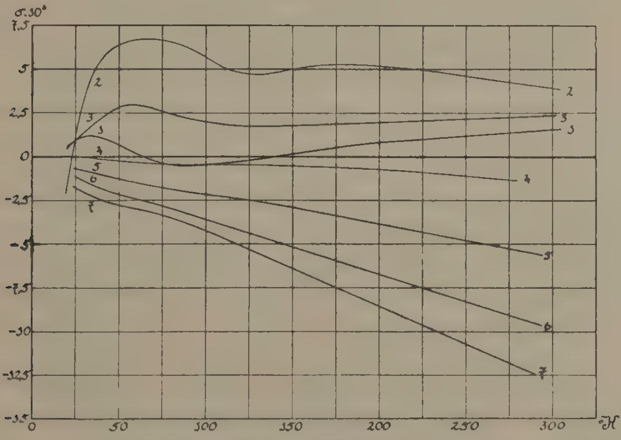

Fig. 7. THOMSON-effect for *Cu*-alloys.

1. *Cu* (techn. pure)
2. *Cu* + 0.075 *At* % *Fe*
3. „ „ 0.35 *At* % *Au*
   (copperalloy normal)
4. *Cu* + 0.35 *At* % *As*
5. „ „ 1.0 *At* % *Ni*
6. „ „ 2.0 „ „ „
7. „ „ 3.0 „ „ „

Figs. 7 and 8. As the values of the three *CuAs*- and the two *CuFe*-alloys almost coincide, the curve of one alloy has been traced for each of them.

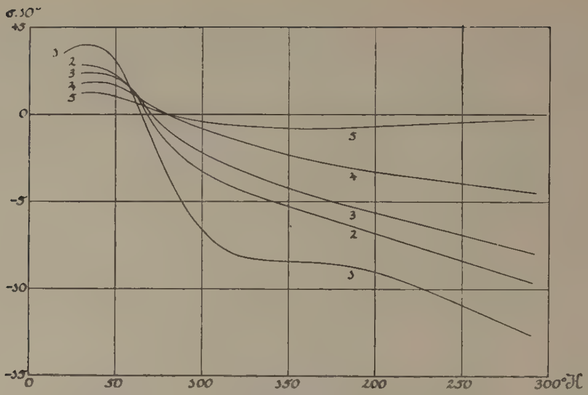

Fig. 8. THOMSON-effect for *PtRh*-alloys.

1. *Pt* pure
2. *Pt* + 1.9 *At* $^0/_0$ *Rh*
3. „ „ 3.5 „ „ „
4. *Pt* + 9.1 *At* $^0/_0$ *Rh*
5. „ „ 17.4 „ „ „ (10 weight $^0/_0$).

TABLE III. Thomsoneffect in Microvolt per degree.

T	Copperalloys					
	1.1 *At* $^0/_0$ *Ni*	2.2 *At* $^0/_0$ *Ni*	3.3 *At* $^0/_0$ *Ni*	0.075 *At* $^0/_0$ *Fe*	0.51 *At* $^0/_0$ *As*	1.35 *At* $^0/_0$ *As*
20	—	—	—	—1.7	—	—
30	—0.80	—1.40	—2.05	+3.3	+0.27	0.00
40	1.05	1.85	2.5	5.65	0.12	—0.15
50	1.3	2.15	2.8	6.35	—0.07	0.28
60	1.5	2.4	3.0	6.65	0.28	0.30
70	1.7	2.7	3.2	6.7	0.44	0.40
80	1.85	2.95	3.5	6.6	0.60	0.45
90	2.0	3.3	3.85	6.2	0.62	0.43
100	2.15	3.6	4.25	5.7	0.55	0.43
110	2.3	3.9	4.65	5.1	0.50	0.43
120	2.4	4.2	5.1	4.8	0.54	0.45
130	2.6	4.5	5.5	4.7	0.55	0.50
140	2.7	4.85	5.95	4.8	0.55	0.53
150	2.9	5.15	6.4	5.0	0.56	0.55
160	3.1	5.45	6.8	5.15	0.57	0.57
170	3.3	5.8	7.25	5.25	0.60	0.60
180	3.45	6.1	7.7	5.25	0.61	0.65
200	3.85	6.7	8.55	5.2	0.65	0.75
220	4.25	7.35	9.4	5.0	0.70	0.87
240	4.6	8.0	10.3	4.7	0.74	1.05
260	5.0	8.6	11.15	4.4	0.78	1.20
280	5.35	9.2	12.0	4.15	0.82	1.40
300	—	—	—	3.9	—	—

TABLE IV. THOMSON-effect in Microvolt per degree.

T	Platinumalloys			
	1.9 *At* % *Rh*	3.5 *At* % *Rh*	9.1 *At* % *Rh*	17.4 *At* % *Rh*
30	+2.85	+2.45	+1.75	+1.2
40	2.7	2.35	1.85	1.25
50	2.25	2.1	1.65	1.0
60	1.3	1.4	1.15	0.7
70	—0.3	0.2	0.5	0.35
80	1.6	—0.9	±0.0	±0.0
90	2.55	1.5	—0.45	—0.25
100	3.3	2.2	0.85	0.4
110	3.8	2.7	1.15	0.55
120	4.25	3.1	1.5	0.65
130	4.6	3.5	1.75	0.7
140	4.95	3.9	2.05	0.75
150	5.3	4.25	2.35	0.8
160	5.6	4.55	2.55	0.8
170	5.9	4.85	2.8	0.8
180	6.2	5.1	3.0	0.8
200	6.8	5.65	3.3	0.7
220	7.45	6.15	3.6	0.6
240	8.05	6.65	3.85	0.5
260	8.7	7.15	4.1	0.4
280	9.2	8.65	4.35	0.35

§ 4. *Thermo-electric Force per Degree for Alloys at corresponding Temperatures.* Table V gives for every 20 degrees the thermo-electric force per degree for the alloys mentioned against the silveralloy mentioned in § 1. The values were obtained from curves drawn through the experimental points.

§ 5. *Final remarks.* Earlier measurements of thermo-electric force have shown that different investigations often give very divergent results, especially at the lowest temperatures. Our researches on dilute alloys also prove that the thermo-electric qualities are in certain cases essentially changed even by a very small admixture of a foreign metal. An investigation of the pure metals requires a material that is free from impurities to the highest possible extent. Also differences in cold-working and annealing have a great influence. In regard to this it is unsuitable to operate with very thin wires, which is also shown by the fact, that WIETZEL [1]) by using *Pt*-wires of 0.05 mm diameter (pure *Pt* from HERAEUS) obtained very

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[1]) G. WIETZEL. Ann. d. Phys. (4) 43, 605, 1914.

TABLE V. Thermoelectric Force in Microvolt per degree against silveralloy.

t °C	Copperalloys												
	1.12 *At* % *Ni*	2.16 *At* % *Ni*	3.32 *At* % *Ni*	3.32 *At* % *Ni* 1)	0.075 *At* % *Fe*	0.17 *At* % *Fe*	0.09 *At* % *Co*	1.01 *At* % *Pd*	1.99 *At* % *Pd*	3.01 *At* % *Pd*	0.51 *At* % *As*	1.01 *At* % *As*	1.35 *At* % *As*
—255	—2.00	—1.95	—1.75	—1.75	—15.75	—	—	—	—	—	—0.39	—0.31	—0.31
240	2.50	2.80	2.85	2.85	15.15	—	—	—	—	—	0.38	0.43	0.46
220	3.10	3.70	4.05	4.05	12.40	—	—	—	—	—	0.38	0.52	0.57
200	3.60	4.55	5.05	5.15	10.30	—	—	—1.00	—1.38	—1.46	0.47	0.63	0.68
180	4.10	5.40	6.00	6.20	8.70	—9.20	—7.65	1.01	1.43	1.56	0.64	0.78	0.82
160	4.60	6.15	6.90	7.25	7.75	8.50	8.30	1.02	1.48	1.66	0.79	0.90	0.94
140	5.05	6.90	7.80	8.35	7.00	7.75	8.70	1.04	1.54	1.76	0.94	1.02	1.08
120	5.50	7.60	8.70	9.35	6.40	7.15	9.00	1.04	1.58	1.85	—	—	—
100	6.00	8.40	9.65	10.45	5.85	6.70	9.40	1.06	1.63	1.94	—	—	—
80	6.45	9.10	10.60	11.55	5.35	6.40	9.75	1.07	1.68	2.02	1.40	1.48	1.53
60	6.95	9.85	11.50	12.55	4.95	6.10	10.00	1.09	1.74	2.12	1.55	1.63	1.70
40	7.35	10.60	12.40	13.65	4.60	5.80	10.30	1.11	1.80	2.24	1.70	1.81	1.88
20	7.80	11.35	13.30	14.70	4.30	5.55	10.40	1.14	1.86	2.37	1.85	1.98	2.06
0	8.20	12.05	14.20	15.75	4.10	5.25	10.80	1.16	1.94	2.50	2.03	2.16	2.24
+20	8.70	12.80	15.15	16.80	3.90	5.05	10.95	1.18	2.01	2.62	2.16	2.34	2.43

1) Heated to 700 °C.

TABLE V (*continued*).

t °C	Platinumalloys			
	1.9 *At* % *Rh*	3.5 *At* % *Rh*	9.1 *At* % *Rh*	17.4 *At* % *Rh*
—255	+1.10	+1.00	+0.80	+0.60
240	2.70	2.30	1.70	1.20
220	3.85	3.40	2.50	1.60
200	4.20	3.70	2.80	1.85
180	3.65	3.30	2.65	1.80
160	2.90	2.85	2.45	1.70
140	2.20	2.30	2.15	1.60
120	1.35	1.65	1.80	1.40
100	0.55	0.95	1.40	1.15
80	—0.20	0.35	1.00	0.90
60	0.95	—0.30	0.55	0.70
40	1.70	0.95	0.15	0.50
20	2.50	1.60	—0.25	0.45
0	3.25	2.20	0.65	0.35
+20	4.00	2.85	1.05	0.25

varying results in different measurement-series. Our measurements on different pieces of the copper wire used or the copperalloy wire show however (Tab. I and II of the former paper) that it is possible to get reproduceable values if only the material is well-defined. This also follows from the investigations of the LE CHATELIER-element (*Pt* + 17.4 *At* % *Rh* against *Pt*) that have been performed by WIETZEL as well as by us. The wires used, which probably are of the same origin (HERAEUS) give in both cases results agreeing almost completely. This fact together with the possibility of getting high thermo-electric forces per degree at low temperatures for instance by adding small quantities of iron to copper seems to us to be of importance for measuring low temperatures with thermo-elements.

§ 6. *Conclusion.* As for the pure metals (see the former paper) so we conclude for the alloys experimented with, that in general they seem to have a tendency towards verification of the limiting laws $\sigma \rightarrow 0$ and $e \rightarrow 0$ for $T \rightarrow 0$, especially as regards the THOMSON-effect. Here too experiments at still lower temperatures will be necessary to obtain conclusive results.

Physics. — *Temperaturbestimmung im elektrischen Bogen aus dem Bandenspektrum.* Von L. S. ORNSTEIN und W. R. VAN WIJK.

(Communicated at the meeting of January 25, 1930).

Wenn man annimmt dass die im Lichtbogen emittierten Bandenspektren eine Verteilung der Rotationszustände aufweisen, welche der wirklichen Temperatur des Gases an der Emissionsstelle entspricht, so kann man aus den Intensitätsverhältnissen der Bandenlinien zu einander diese Temperatur berechnen.

BIRGE hat schon vor einigen Jahren mit Hilfe dieser Ueberlegung aus der Lage des Maximums in der Cyanbande 3883 eine Temperaturbestimmung im Bogen durchgeführt.

Es ist aber viel besser zu diesem Zweck Intensitätsmessungen anzustellen und das nicht nur wegen des Vorteils dass jedes gemessene Linienpaar eine unabhängige Neubestimmung der effektiven Temperatur liefert, sondern auch weil die Linien im Maximum einander überdecken können und speziell weil eine Abweichung von der Temperaturverteilung direkt beobachtbar wird.

Wenn eine solche Abweichung in der Verteilung der Linienintensitäten vorliegt so bedeutet das noch nicht dass auch wirklich die Anzahl der Rotationsterme nicht durch die Gastemperatur bestimmt ist.

Ein solcher Effekt tritt nämlich auch dann auf wenn die Temperatur der leuchtende Schicht nicht überall gleich ist.

Im letzten Falle hat die Stelle, wo das Maximum auftritt, nichts mit der Temperatur zu tun, sondern hängt von der zufälligen Verteilung ab.

Der Einfluss einer nicht mit überall gleicher Temperatur leuchtenden Gasschicht wird derartig sein dass für die höheren Rotationszustände auch eine höhere Verteilungstemperatur wirksam ist als für die niedrigeren, dass also die Bande langsamer vom Maximum der Intensität abfällt als man aus dem Austieg erwarten würde.

In dieser Tatsache könnte vielleicht in manchen Fällen die Ursache der von vielen Autoren erwähnten „Bevorzügung" der höheren Quantenzahlen liegen. Der Verteilungsmodul der höheren Rotationsterme würde dann etwa der Maximaltemperatur der Gasschicht entsprechen.

In dieser Arbeit wurde versucht die Temperatur in den inneren und äusseren Schichten eines Lichtbogens zu messen.

Es wurde dafür gesorgt dass an den erwähnten Stellen ein anderes Bandenspektrum emittiert wurde, wodurch die Temperatur von beiden Teilen gesondert untersucht worden könnte.

Dazu wurde der Bogen zwischen einem Aluminiumstab als Kathode und Kohle als Anode erzeugt.

Der Lichtbogen besteht in diesem Fall aus einem violetten Kern (Cyanbanden) der durch eine grüne Hülle (AlO-Banden) umsaumt ist.

Einmal wurde eine Aufnahme gemacht wobei nur der äuszerste Rand des Bogens auf dem Spalt abgebildet war (nur AlO Spektrum) das andere Mal wurde der innere Kern des Bogens photographiert (AlO + CN Spektrum). Nach den üblichen Utrechter Methoden wurden die Intensitätsmarken aufgenommen und die Platten durchphotometriert.

Die violette Cyanbanden und die grüne Aluminiumbanden sind vom selben Typus $^2\Sigma \rightarrow {}^2\Sigma$.

Für diesen Fall sind die Intensitäten der n^{te} P und R Linie wenn die Feinstruktur der einzelnen Linien ausser Betracht gelassen wird proportional zu n.

Weil die n^{te} P Linie vom $(n-1)^{\text{ten}}$ Energieterm ausgeht, die n^{te} R Linie vom n^{ten}, wird im Falle einer Boltzmannschen Verteilung $\log \frac{Ip(n)}{n}$ proportional zu

$$-\frac{h^2}{8\pi^2 J}\,\frac{n(n-1)}{kT}$$

(J Trägheitsmoment, k Boltzmannsche Konstante, T absolute Temperatur).

In der untenstehenden graphischen Darstellung ist als Ordinate $\log \frac{Ir(n)}{n}$ b.z.w. $\log \frac{Ip(n+1)}{n+1}$ aufgetragen als Absisse $n\,(n+1)$.

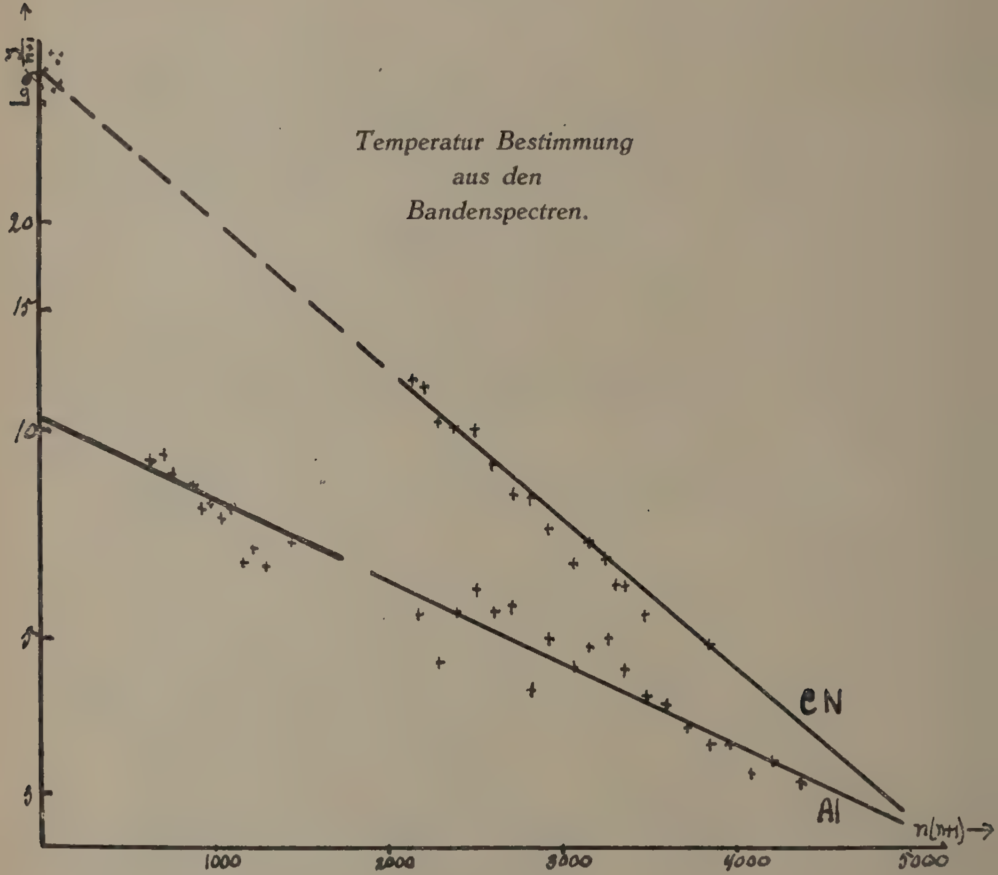
Wo I die Intensität der betreffenden Linie darstellt.

Man sieht dass für die hohen Rotationen eine mit guter Annäherung gerade Linie durch die Beobachtungspunkte gelegt werden kann; dass aber in der CN Bande anscheinend nicht für alle Rotationen dieselbe wirksame Temperatur besteht.

Die Linien mit niedrigen Laufzahl in der AlO Bande könnten mit der benutzen Dispersion (6 M. Gitter 1$^{\text{er}}$ Ordnung) nicht für die Messung genügend aufgelöst erhalten werden. Die der Cyanbande sind auch ziemlich stark überlagert.

Die Verteilungstemperatur welche aus den hohen Rotationstermen abgeleitet wird und die man etwa als Maximaltemperatur der leuchtenden Schicht ansehen kann, berechnet sich aus der graphischen Darstellung zu 5000° abs. für CN und 2800° abs. für AlO, wobei ein Lichtbogen von 1 bis 1.5 cm. Polabstand mit einer Stromstärke von 9 A. bei einer Spannung von 220 V. benutzt wurde.

Es wird interessant sein Art und Weise wie die gemessene Temperatur von den Bedingungen abhangen zu untersuchen. Messungen zu diesem Zweck sind im Gange.



Temperatur Bestimmung
aus den
Bandenspectren.

Fig. 1.

Utrecht, Jan. '30.

Mathematics. — *Die Endlichkeit der Invarianten bei Eingliedrigen Gruppen.* Von R. WEITZENBÖCK.

(Communicated at the meeting of January 25, 1930).

Es sei $f(x)$ eine Form der n Variabeln $x_1, x_2, \ldots, x_n$ und $A = \| a_i^k \|$ eine n-dimensionale Matrix mit dem Wurzeln λ_i (= Wurzeln der Gleichung n-ten Grades $Det\,|\lambda E - A| = 0$). Die Koeffizienten von $f(x)$ und die Elemente a_i^k von A seien gewöhnliche komplexe Zahlen; etwas allgemeiner kann man diese Koeffizienten, die a_i^k und die Wurzeln λ_i als Elemente eines festen Körpers voraussetzen.

Der Matrix A ist eindeutig zugeordnet die infinitesimale Transformation

$$A(f) = \frac{\partial f}{\partial x_i} a_i^k x_k = \sum_{i=1}^{n} \frac{\partial f}{\partial x_i} \sum_{k=1}^{n} a_i^k x_k .$$

Gilt für eine Form $f(x) \neq 0$ identisch in den x_i die Beziehung

$$A(f) = \alpha . f,$$

so nennen wir f eine *A-Invariante*. Wir werden dann folgenden Satz beweisen:

Alle A-Invarianten besitzen eine endliche Integritätsbasis $f_1, f_2, \ldots, f_s$ $(1 \leqq s \leqq n)$, *sodass also jede A-Invariante* $f(x)$ *ein Polynom dieser Basisinvarianten wird:* $f(x) = P(f_1, f_2, \ldots, f_s)$.

§ 1.

Wir suchen zuerst die linearen A-Invarianten. Ist

$$Det\,|\lambda E - A| = (\lambda - \lambda_1)^{\nu_1} (\lambda - \lambda_2)^{\nu_2} \ldots (\lambda - \lambda_h)^{\nu_h} = 0 \quad . \quad . \quad (1)$$

die karakteristische Gleichung der Matrix A, wobei $\lambda_i \neq \lambda_k$ und $\nu_1 + \nu_2 + \nu_3 + \ldots + \nu_h = n$ ist, so sind $\lambda_1, \lambda_2, \ldots, \lambda_h$ die $h \geqq 1$ untereinander verschiedenen Wurzeln der Matrix A. Es gibt dann eine lineare, umkehrbare Transformation $y = S(x)$, bei welcher A in die Normalform $N = S^{-1} A S$ übergeht[1], die wir, um die weiter folgende Ableitung nicht allzu verwickelt zu gestalten, in der speziellen Form gebrauchen:

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[1] H. E. HAWKES, Amer. Journal of Math. **32** (1910), p. 101—114.

$$\bar{y}_i = n_i^k \, y_k \qquad \varepsilon_i = \eta_k = \ldots = 1 \qquad 0 \leqq \mu_i \leqq \nu_i - 1$$

$$N = \left\| \begin{array}{ccccc|ccc} \lambda_1 & \varepsilon_1 & & & & & & \\ & \lambda_1 & \varepsilon_2 & & & & & \\ & & \ddots & & & & & \\ & & \lambda_1 & \varepsilon_{\mu_1} & & & & \\ & & & \lambda_1 & & & & \\ & & & & \ddots & & & \\ & & & & \lambda_1 & & & \\ \hline & & & & & \lambda_2 & \eta_1 & \\ & & & & & & \lambda_2 & \eta_2 \\ & & & & & & & \ddots \end{array} \right\| = \| n_i^k \| ; \quad \ldots \ldots \quad (2)$$

N setzt sich längs der Hauptdiagonale zusammen aus h quadratischen Matrizen N_{ν_i} der Seitenlänge ν_i; alle nicht angeschriebenen Elemente sind Null, λ_i kann ebenfalls Null sein [1]).

Die A-Invarianten $f(x)$ gehen jetzt über in N-Invarianten $g(y)$ und es genügt obigen Satz für die N-Invarianten zu beweisen.

Soll $m^i y_i = \sum\limits_{i=1}^{n} m^i y_i$ eine lineare Invariante sein, so müssen identisch in allen y_i die Gleichungen

$$m^i \bar{y}_i = \varphi(n_i^k) \, . \, m^i y_i$$

gelten. Dies gibt nach (2):

$$\left.\begin{array}{r} m^1 \lambda_1 = \varphi \, . \, m^1 \\ m^1 + m^2 \lambda_1 = \varphi \, . \, m^2 \\ m^2 + m^3 \lambda_1 = \varphi \, . \, m^3 \\ \ldots\ldots\ldots \end{array}\right\} \quad \ldots\ldots\ldots \quad (3)$$

Hieraus findet man, dass nur diejenigen m^i nicht Null sein müssen, wofür in der i-ten Zeile von (2) nur λ_j und keine Eins vorhanden ist. Es sind also

$$y_{\mu_1+1}, \; y_{\mu_1+2}, \ldots, y_{\nu_1} \quad ; \quad y_{\nu_1+\mu_2+1}, \ldots, y_{\nu_1+\nu_2} ; \quad \ldots \quad (4)$$

lineare N-Invarianten und jede andere lineare N-Invariante ist linear und homogen durch diese ausdrückbar. Sind daher z.B. alle $\mu_i = 0$, d.h. stehen in der Normalform (2) keine Einsen, so haben wir n lineare N-Invarianten y_i und der Satz ist bewiesen.

§ 2.

Enthält die Normalform (2) auch Einsen, so kommen zu den linearen N-Invarianten (4) weitere, nicht-lineare hinzu.

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[1]) Bei der allgemeinen Normalform stehen die Einsen ε_i, η_k, ... in den N_{ν_i} auch unmittelbar rechts der Hauptdiagonale, aber in anderer Anordnung.

Sei nämlich $g(y) = \Sigma\, g_{p_1 p_2 \dots p_n}\, y_1^{p_1}\, y_2^{p_2} \dots y_n^{p_n}$ eine N-Invariante; dann gibt die Forderung

$$N(g) = (p_1\, \lambda_1 + \dots + p_n\, \lambda_h) \cdot g$$

die Gleichung

$$\sum_{N_{\nu_i}} \left(\frac{\partial g}{\partial y_1} \cdot y_2 + \frac{\partial g}{\partial y_2} \cdot y_3 + \dots + \frac{\partial g}{\partial y_{\mu_1}} \cdot y_{\mu_1+1} \right) = 0 \quad . \;\; . \;\; . \quad (5)$$

wo die Summe über alle die Teilmatrizes N_{ν_i} von N zu erstrecken ist, für die $\mu_i \neq 0$ ist. Bezeichnen wir der grösseren Deutlichkeit halber

$$y_{\nu_1+1}\,,\; y_{\nu_1+2}\,,\, \dots\,,\, y_{\nu_1+\nu_2} \quad \text{mit} \quad z_1\,,\; z_2\,,\, \dots\,,\, z_{\nu_2}$$

$$y_{\nu_1+\nu_2+1}\,,\; y_{\nu_1+\nu_2+2}\,,\, \dots\,,\, y_{\nu_1+\nu_2+\nu_3} \quad \text{mit} \quad t_1\,,\; t_2\,,\, \dots\,,\, t_{\nu_3} \quad \text{u.s.f.,}$$

so lautet (5):

$$\left(\frac{\partial g}{\partial y_1} \cdot y_2 + \dots + \frac{\partial g}{\partial y_{\mu_1}} \cdot y_{\mu_1+1} \right) + \left(\frac{\partial g}{\partial z_1} \cdot z_2 + \dots + \frac{\partial g}{\partial z_{\mu_2}} \cdot z_{\mu_2+1} \right) + \dots = 0 \quad (6)$$

Wir betrachten zuerst die zur Teilmatrix N_{ν_1} gehörige Differentialgleichung, indem wir einfachheitshalber μ statt μ_1 schreiben:

$$\frac{\partial g}{\partial y_1} \cdot y_2 + \frac{\partial g}{\partial y_2} \cdot y_3 + \dots + \frac{\partial g}{\partial y_\mu} \cdot y_{\mu+1} = 0 \quad . \;\; . \;\; . \;\; . \;\; . \quad (7)$$

Ihr allgemeines, ganz-rationales Integral ist leicht anzugeben. Es ist ein Polynom der partikulären, untereinander unabhängigen Lösungen

$$\left.\begin{aligned}
C_1 &= y_{\mu+1} \\
C_2 &= y_{\mu-1}\, y_{\mu+1} - \frac{1}{2}\, y_\mu^2 \\
C_3 &= y_{\mu-2}\, y_{\mu+1}^2 - y_{\mu-1}\, y_\mu\, y_{\mu+1} + \frac{1}{3}\, y_\mu^3 \\
C_4 &= y_{\mu-3}\, y_{\mu+1}^3 - y_{\mu-2}\, y_\mu\, y_{\mu+1}^2 + \frac{1}{2}\, y_{\mu-1}\, y_\mu^2\, y_{\mu+1} - \frac{1}{8}\, y_\mu^4 \\
&\qquad \text{u.s.f.}
\end{aligned}\right\} \; . \;\; . \quad (8)$$

wobei C_m für $3 \leqslant m \leqslant \mu$ durch die Rekursionsformel gegeben wird:

$$\left.\begin{aligned}
C_m = y_{\mu-m+1}\, y_{\mu+1}^{m-1} - y_\mu\, C_{m-1} - \frac{1}{2!}\, y_\mu^2\, C_{m-2} - \frac{1}{3!}\, y_\mu^3\, C_{m-3} - \dots - \\
- \frac{1}{(m-2)!}\, y_\mu^{m-2}\, C_2 - \frac{1}{m!}\, y_\mu^m .
\end{aligned}\right\} \quad (9)$$

Analog zu (8) erhält man mit den $\mu_2 + 1$ Veränderlichen z_i die Invarianten $C_1' = z_{\mu_2+1}, C_2', \dots, C_{\mu_2}'$ u.s.f. für jede der Teilmatrizes N_ν .

Führt man diese Formen $C_i, C_i', \ldots$ als neue Veränderliche in (6) ein, so reduziert sich diese Differentialgleichung auf:

$$\frac{\partial g}{\partial y_{\mu_1}} \cdot y_{\mu_1+1} + \frac{\partial g}{\partial z_{\mu_2}} \cdot z_{\mu_2+1} + \frac{\partial g}{\partial t_{\mu_3}} \cdot t_{\mu_3+1} + \ldots = 0 \quad . \quad . \quad . \quad (10)$$

Das allgemeine ganz-rationale Integral dieser Gleichung (10) ist ein Polynom der zweireihigen Determinanten

$$\triangle_{12} = y_{\mu_1} z_{\mu_2+1} - z_{\mu_2} y_{\mu_1+1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

der Matrix:

$$\left\| \begin{matrix} y_{\mu_1} & z_{\mu_2} & t_{\mu_3} & \ldots \\ y_{\mu_1+1} & z_{\mu_2+1} & t_{\mu_3+1} & \ldots \end{matrix} \right\| \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Fassen wir zusammen: Jede ganze rationale N-Invariante $g(y)$ ist ein Polynom der Basisinvarianten von dreierlei Typus:

1. die linearen Invarianten $y_{\mu_1+1}, \ldots, y_{\nu_1};\ z_{\mu_2+1}, \ldots, z_{\nu_2}; \ldots$
2. die Formen $C_i, C_i', \ldots$ (vgl. (8)) für $i \geqq 2$.
3. die quadratischen Invarianten $\triangle_{ik}$ (vgl. (12)).

Bacteriology. — *The bacteriophage of Bac. megatherium: a product of the living bacterial cell.* By L. E. DEN DOOREN DE JONG. (Communicated by Prof. A. J. KLUYVER.)

(Communicated at the meeting of January 25, 1930).

In 1925 and '26 SÖHNGEN and GRIJNS [1]) studied in detail the bacteriophage of *Bac. danicus* LÖHNIS et WESTERMANN, a sporeforming bacterium, according to BEIJERINCK one of the many varieties of the wellknown *Bac. megatherium* DE BARY. In these interesting studies much attention was paid to the thermal deathtime of the bacteriophage of *Bac. danicus*. It may be stated here that the authors concluded from their experiments, that the form of the thermal death-curve neither proved nor disproved the ultra-microbial nature of the phage.

The fact that here for the first time [2]) the phenomenon of bacteriophagy has been observed with a sporeforming bacterium, now makes it possible to settle the dispute which immediately arose after the discovery of the bacteriophage by D'HERELLE, that is the controversy whether the bacteriophage must be considered as an ultramicrobe or as a product of the bacteria themselves.

Indeed, more than one symptom has pointed to the latter possibility. So for instance more than once mention was made in literature of bacterial cultures that spontaneously showed bacteriophagy [3]).

D'HERELLE and his followers, who have always stuck to D'HERELLE's original theory of the ultramicrobial nature of the phage, removed the difficulty ensuing from spontaneous bacteriophagy by assuming the hypothesis, that such a culture was already latently infected with the bacteriophage from the origin. As with the asporogen bacteria, it was not possible to free them with perfect certainty of a possibly present phage, little could be said against this argument.

This situation has changed with the discovery of the susceptibility of sporeforming bacteria to bacteriophagy. As it is a wellknown fact that the phages, just as the enzymes, are readily destroyed at temperatures between 60° C. and 75° C. and since the bacilli, owing to their capacity of forming spores, can easily resist temperatures "fatal" to the phages, it has now become possible to bring about the said purification.

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[1]) N. L. SÖHNGEN en A. GRIJNS, Versl. Kon. Akad. v. Wet. Amsterdam, **34** (1925) p. 983.

A. GRIJNS, Waarnemingen omtrent den bacteriophaag bij *Bac. danicus* en *B. radicicola* Diss. Wageningen (1926).

[2]) However it must be observed that D'HERELLE (Le Bactériophage et son comportement, 2ième Ed. Paris 1926) on p. 239 devotes a few lines to the bacteriophagy of the sporeforming *Bac. subtilis*.

[3]) C.f. D'HERELLE, l.c. p. 208—213; p. 293.

So at present bacterial cultures can be obtained that are entirely free of "latent" bacteriophages. If in some way or other it should appear, that in such a "dephagenised" culture bacteriophagy could be brought about without the cooperation of other living agentia, this would furnish a decisive argument against the ultramicrobial nature of the bacteriophage. In the following an account is given of investigations which aimed at experimentally testing this possibility.

In order to treat the problem as generally as possible, I made use of strains of *Bac. megatherium*, which I had isolated in different ways, from garden-soil and other materials [1]). The strains that were first investigated were numbered 333 up to and including 338.

Manifoldly repeated experiments to which I shall return in a more detailed communication elsewhere showed that when these strains — if originating from culture tubes that were some months old — were spread on ordinary (1 %) peptoneagar [2]) (2 % agar) there resulted either strongly speckled colonies on the plates or a mixture of opaque and more or less transparent colonies. It appeared that the speckles as well as the more transparent colonies were formed by a non-sporeforming mutilate [3]) of the bacillus. The opaque colonies (or parts of colonies), however, were built up from the sporeforming cells (principal-form). In future this principal-form will be indicated as the a-state of the bacterium, the sporeless mutilate as the *b*-state. In the following experiments two typical strains, that is of *Bac. megatherium* 337 (speckle-forming) and of 338 (casting off transparent colonies), have been used. The *b*-state of these strains could easily be brought into pure culture. They turned out to have the remarkable property of becoming every day more transparent (the colonies as well as the cells themselves), while they lost their colour (they often were yellow or yellowish), and died after about 10 or 14 days. In the agar there often appeared diffuse rings round the colonies.

All this pointed out that these (*b*) cells were subject to lytic actions. As it was possible that the bacteriophage brought about this lysis, the mutilates (*b*) were inoculated into 1 % peptonewater and incubated at 28° C. for some time. After filtration of the culture-liquid it appeared, however, that the filtrate did not clear bacterial suspensions of 337*a* and -*b* or of 338*a* and -*b*. Neither was it capable of giving rise to "plaques" in spreadings of said bacteria on plates with 1.5 % agar, 1 % peptone and 0.1 % glucose.

Previous researches concerning the nutrition of sporeforming bacteria had taught me that, on nutrient media containing a high percentage of peptone, they were no more capable of forming spores. Even within a very short space of time, practically all the cells lost their power to form spores and so were forced to pass irreversibly from the *a*- into the *b*-state.

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[1]) An accumulation method of *Bac. megatherium* will be described elsewhere.

[2]) In all the tests the excellent peptone "Poulenc" was used.

[3]) For the use of the term "mutilation" c.f. J. J. VAN LOGHEM, Ned. Tijdschr. v. Geneesk. **73**, p. 655 (1929).

Making use of the above, I suspended the strains 337*a* and 338*a* in 1 % peptonewater, pasteurized them during 10′ at 90° C. and thereupon put them on 10 % peptoneagar, in order to force them to mutilate into the *b*-state.

Indeed, already in a few days mutilates could be obtained which showed the same properties as those *b*-strains which were isolated before the pasteurization.

So we may conclude that the described lytic action is quite independent of a preceding pasteurization of the original culture from which the mutilates originate.

Though up to now from the six *Megatherium*-strains which I had taken into examination, I had not succeeded in obtaining mutilates, containing a lysin, that could be separated from the cell by filtration, I was not discouraged and in December 1929 I tested a dozen other strains (numbered 891 up to 902 inclusive). With exception of strain 902 (= *Bac. danicus*) [1]) they had been isolated some months before.

These strains, of which the cultures were about three or four months old, were all spread on ordinary peptoneagar to examine their susceptibility to mutilation. It appeared that the greater part of them gave transparent mutilates: besides opaque grey to brown sporogen colonies, most of the strains yielded a small number of more transparent, sometimes coloured colonies, that were built up out of the sporeless form of the *Megatherium*-cell. There were also several strains the opaque colonies of which had transparent speckles. So at first sight there was no difference between any of them and the strains 333 up to 338 inclusive. However, this changed when the plates were kept a little longer. Just as was the case with 337*b* and 338*b*, the colonies of the mutilates daily grew more transparent, but one strain, namely 899 drew my special attention by a rapid formation of socalled "Flatterkolonien". The outline of these asporogen colonies did not remain completely entire as was the case with the *b*-state of all the other strains. The colonies of this particular strain were strongly affected: there appeared incisions that sometimes went so deep, that in a short time the colonies wasted away. Other colonies, however, remained unimpaired, but became transparent at an extraordinarily rapid rate and got a diffuse ring round the colony; it was as if they were dissolved in the agar.

In such cases they already died within four days. If they were transferred, there appeared colonies that were also strongly affected. But there were also 899*b*-colonies, that were much more resistant to the lysis and that could grow out to a fairly developed yellow colony. In the long run pits and holes were formed in these colonies.

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[1]) Received from Prof. BEIJERINCK.

A microscopical examination of the young cultures of 899*b* also showed sporeless *Megatherium*-rods, some locally much swollen, others again quite round as if they were subjected to an internal tension. But it was especially noteworthy that many cells under these normal conditions of nutrition had been decomposed into a granular mass in such a way, that only a small part of the outer cellular wall had remained.

The sporogen 899*a* state is much less interesting, because the greater part of the colonies is not or little affected. The microscopical preparation shows granular, later spore-bearing, cells and finally nothing else but spores.

The extraordinary degree in which the lytic phenomena demonstrated themselves in the *b*-state of this *Megatherium* 899, gave rise to the expectation that in this case the lytic principle might prove to be filterable.

However experiments on the lytic capacity of the filtrate of 899 *b*-cultures in peptone-broth on suspensions of 899*a* cells were not quite successful. As moreover 899*b* cells could not be used as testmaterial by reason of their autophageous properties, the idea struck me to use the *b*-states of the formerly described relatively resistant strains as such.

Here it must be emphasized that the *b*-cultures of the strains 337 and 338 had also been derived from carefully pasteurized cultures.

It appeared from several preliminary experiments that not only bacterial suspensions of 337*b* and 388*b* were readily put into lysis by the filtrate, but that also dissemination of this filtrate on plates on which 337*b* or 338*b* were spread, gave rise to the appearance of typical "plaques".

Although this result does not yet suffice to justify the identification of the lytic principle obtained with the bacteriophage — I will revert to this point afterwards — it was necessary to preclude every possibility of the presence of a latent infection of an autonomous ultramicrobial bacteriophage in these experiments. So I thought it advisable first of all to repeat all operations described with the utmost precautions. Strain 899 was heated in tubes with a small quantity of peptonewater with the greatest care in a waterbath respectively 5′ at 80° C., 15′ at 80° C., 5′ at 90° C., 15′ at 90° C., 5′ at 100° C. and 15′ at 100° C.

In the same time portions of a filtrate that on testing had given rise to millions of "plaques" were also exposed to the heating procedures. In all cases the "plaque"-forming capacity of these filtrates was completely destroyed. In a later experiment even a heating at 70° C. during 5′ sufficed to annihilate the lytic principle.

The tubes with the bacterial spores were immediately cooled down after the heating and incubated [1]) during two days at 28° C. Thereupon a small quantity of the contents of each of the tubes was inoculated in a range of tubes with 10 % peptoneagar. After 24 hours the contents of the tubes were examined microscopically and it appeared again, that the cells had made no spores in these culture media. About a week after the inoculation the contents of these culturetubes were spread on plates of peptoneagar. The effectiveness of the cultivation on media with a high percentage of peptone appeared again from the fact, that at least as many mutilated colonies appeared as there were principal-forms. Moreover the transparent colonies of the mutilates were practically all corroded.

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[1]) Immediate spreading on ordinary (1%) peptoneagar exclusively yielded the *a*-state.

Thereupon a corroded colony of a 899*b* mutilate, originating from a culture heated 5′ at 100° C., was inoculated into 1 % peptonewater [1]). After incubation at 28° C. during one day the culture liquid was filtered through a Seitz-filter and the filtrate was added in different dilutions to suspensions of 337*b* and 338*b*, which had also been obtained from pasteurized cultures.

To my great satisfaction I again observed complete clarification of all tubes to which the undiluted filtrate was added, but even in a dilution of 10^{-6} and 10^{-7} a perfect clearing occurred.

Moreover when the filtrate was put in different dilutions on spreadings of 337*b* and 338*b* there appeared typical "plaques" within 24 hours. The titre proved to be so high that at dilutions of 10^{-1}, 10^{-2} and even 10^{-3} the plate became practically sterile and that at 10^{-5} still thousands of "plaques" could be counted.

Until now it could be considered proved that it is possible to derive from a bacterial cell originating from a spore, that had been subjected to a heating of 5′ at 100° C., a lytic principle that was of a corpuscular nature.

To furnish the complete proof that this principle may be identified with the bacteriophage of d'Herelle it was extremely desirable to show once more quite distinctly that by the lytic action of one of these corpuscules on living bacteria new corpuscules with the same properties originated.

To this end one "plaque" was dug out of the agar and transferred to a suspension of 338*b* in peptone-water. A perfect clearing occurred within one day. The liquid was then filtered and the filtrate after subsequent dilution was brought again on plates of 338*b*. It appeared that after this procedure the original "plaque" gave rise to millions of new "plaques".

Herewith it has been proved that the lytic principle in question has all properties in common with d'Herelle's bacteriophage.

The foregoing experiments show that d'Herelle's theory of the ultramicrobial nature of the bacteriophage has become untenable; they prove that the bacteriophage is a product of the living bacterial cell.

Keuringsdienst van Waren, Rotterdam.

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[1]) **The culture that was heated during 15′ at 100° C. proved to be dead.**

Histology. — *The behavior of elementary membranes outside the organism from a histologist's point of view.* By M. A. VAN HERWERDEN. (Communicated by Prof. J. BOEKE.)

(Communicated at the meeting of January 25, 1930).

It often happens that between the structure of tissues of living organisms and that of non living material a certain homology can be observed. Non living elementary structures often lend themselves better to analysis. For this reason the histologist and the cytologist pay attention to the conditions which influence polyphasic elementary systems, and to the changes which take place in them. Even with the conviction that along this line of enquiry a complete explanation of the phenomena of life never can be obtained, the investigators occupy themselves with these comparisons. They promise an opportunity to bridge the distance between living and non living material, especially in regard to many reversible conditions. A better insight may be obtained in the dynamics of reversible phenomena in living tissue.

This introduction was necessary in justification of my reasons for the investigation described below.

I got started along this line of research by the accidental microscopical examination of thin floating membranes which form quite spontaneously in old 0.5 procent lysol solutions. The small membranes of this nature, after being collected and rinsed in water, appear under the microscope at high power (f.i. × 480) as having a fine fibrous structure. This fibrous structure persists in water and in glycerine. When however a drop of 0.1 procent acetic acid is touched to the border of the coverslip, the bundles of fine fibres suddenly disappear from view and the membrane suddenly changes into a much larger homogeneous gelatinous mass of great viscosity with very irregular borders. This instantaneous change of the fibrous structure into a gelatinous mass, may be followed under the microscope. Offshots of the material and projections, among which some appear as long threads of different diameter, form at different places of the circumference. The viscous character of the material is clearly shown when bridges, formed between the projecting parts, are ruptured spontaneously, or by artificial traction or pressure (fig. 1).

According to the rate of penetration and the concentration of the acetic acid, locally fine alveolar structures make their appearance, in which a hyaline border may often be observed. Fig. 2*a* represents a fibrous bundle which, after the addition of acetic acid, changes into a gelatinous alveolar mass (2*b*). This change has been observed under the microscope and photographed.

When the bridges between the projections rupture, fine threads sometimes persist which have pencilshaped terminations (fig. 3).

The gelatinous shoots, when they are long, often bend over and break off (fig. 4). Small myeline granules may be observed to slide to and fro

M. A. VAN HERWERDEN: THE BEHAVIOR OF ELEMENTARY MEMBRANES OUTSIDE THE ORGANISM FROM A HISTOLOGIST'S POINT OF VIEW.

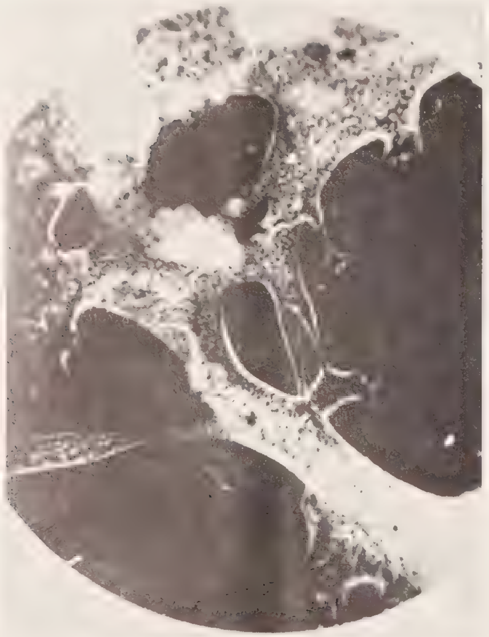

Fig. 1. Fibrous membrane from a lysol solution changed into an alveolar gelatinous mass after treatment with 0.1 procent acetic acid. × 560.

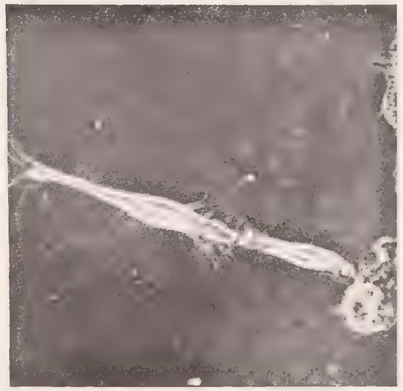

Fig. 3. Pencil shaped projections at the poles of a ruptured bridge, as described in the text. × 560

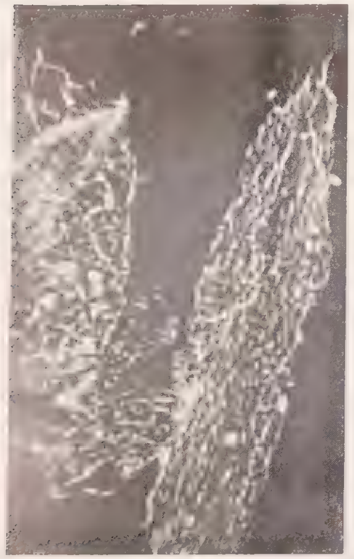

Fig. 2*a*. Fibrous bundle from a lysol membrane. ± × 760

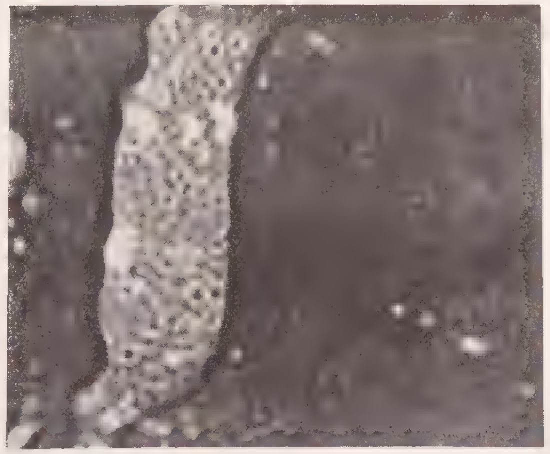

Fig. 2*b*. The same after treatment with 0.1 procent acetic acid. ± × 760

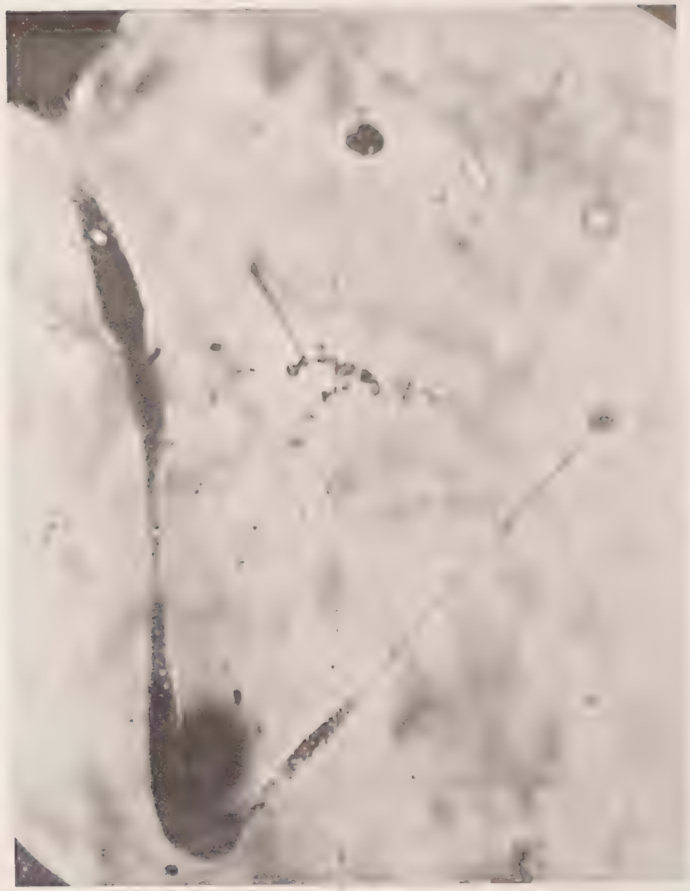

Fig. 4. Curved projecting part of a membrane after treatment with 0.1 procent acetic acid. × 760

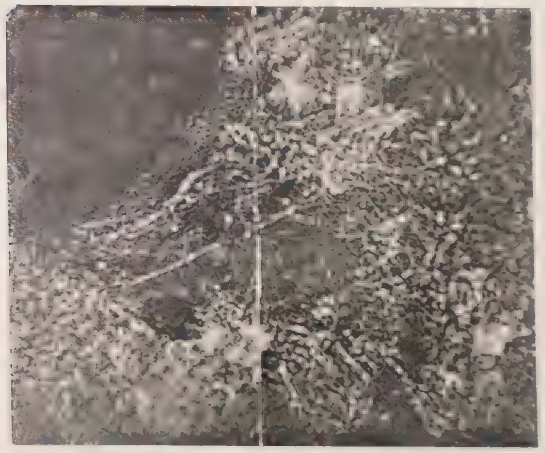

Fig. 5. Reappearance of fibrillary structure in the gelatinous phase after treatment with ammonia. ± × 760.

along these threads, in a way which reminds one of the pictures often seen in tissue cultures where granules move along threads of fibrine or along slender projections of the cells.

After the addition of acetic acid, in several parts of the membrane a threedimensional structure can be recognised. At this stage the altered membrane. which formerly had a fibrous structure, reminds one of a myxomycete plasmodium, seen under the microscope. In other moments, the structures, into which the membranes change when treated with acetic acid, remind one of parts of tissue cultures, such as may be seen e.g. in implantations of bladder-fragments of the frog in lymph, in which transparent membranes extrude from the recently implanted material and rupture again. When a cotton thread lies in the field of vision the alveolar and the hyaline sheets of the altered lysol membranes tend to surround the thread and slide along it, in a way similar to that in which protoplasm of the amoeba slides along the surface of an alga, till the liquid sol phase is suddenly changed into a gel

After the entire membrane has been cleared of fibrillae by the aid of acetic acid, it is sometimes possible to succeed in reversing the process. By rinsing the membrane in 0.5—1 procent ammonia, fibres may reappear in different spots (fig. 5). When the concentration of alkali is too high, it is often possible to observe along the border of the gelatinous mass a phenomenon of "unmixing" which has the character of the phenomena of "coacervation" recently described by H. G. BUNGENBERG DE JONG and H. R. KRUYT [1]). Small pale swollen granules, either singly or assembled in conglomerates, are split off from the crumbling mass at the edge of the gelatinous membrane. In these conditions it sometimes happens that suddenly along the border, large mesomorphic ribbons are formed, which surround the membrane in the form of a fringe. Whereas the membranes in their different modifications are well kept on slides in glycerine during many months without alteration — this fringe of double bounded ribbons is immediately dissolved in glycerine. Sometimes, after addition of ammonia to the membrane in the gelatinous phase, extremely fine regularly placed threads locally appear in polar range When every tiny thread ends in a fine knob at the inner pole, where it is fixed into the underlying substance, the whole resembles the polar arrangement of cilia with their so-called endpieces. As these formations are of a very temporary character, I did not succeed in photographing them.

The different alterations of phase, occurring in the membranes under the influence of acid and alkali, have also been investigated during dark field illumination. Here it often very distinctly appeared that the fibrillae described above, are formed of fine threads arranged in continuous rows. Between and on the fibrillae small gleaming granules are found, showing distinct Brownian movement. As soon as the acetic acid is added, this movement suddenly stops, in consequence of the higher grade of viscosity of the surrounding medium. The fibrillae disappear, small pale stablike particles are now lying quite irregularly dispersed in the groundmass. This groundmass, granular in the beginning of the gelification, finally grows optically empty, bordered however against the surrounding liquid by a distinct clear line. By adding ammonia in low concentration (0.5—1 procent) under the coverslip, one discovers during dark field illumination a local rearrangement of formerly irregularly placed fine pale threads — a local restoration of a fibrillary structure. By the use of a "Wechselcondensor" the dark field observations has been controlled in ordinary light, as far as the necessary magnification allows the use of this condensor.

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[1]) These Proceedings Vol. 32, N⁰. 7, 1929 p. 849.

The addition of bromthymolblue in substance, or in watery solution to a membrane which has been rinsed in water before, enables us to demonstrate the positive charge of the fibrillae: the entire fibrous layer gets a yellow colour. The same is the case with the gelatinous structure, after acetic acid has been added.

Acetic acid increases the positive charge, and in the mean time probably increases the hydration of the micellae. The following discharge by ammonia, with partial dehydration, tends to reestablish the primary condition. However, the former arrangement of large fibrous bundles never has been restored. If the discharge continues, by adding too much ammonia, the phenomenon of "unmixing" (coacervation) sets in.

As well in light — as in dark field, one observes an intense concentration of particles in the border line of the gel, in contrast to the disappearance of particles in the remaining part (fig. 6). With low power during dark field illumination a light border is seen, separating in this phase the membrane with its projections, from the outer medium. With high power a lot of small gleaming particles appear in this border, which sometimes are lying quite irregularly. Sometimes, lying in regular polar arrangement, they give origin to the fringed state described above. Where in the midst of the gelatinous, more or less alveolarly structured mass, small vacuoles are formed, these vacuoles are limited by a sharp borderline from the surrounding substance (fig. 6). The same may be observed in the pulsatory vacuoles of Protozoa, where often attention has been paid by investigators to the reestablishment of the borderline after the evacuation of the vacuolar liquor. There is every reason to believe that — comparable with the here found structures —, in the polyphasic protoplasma, the vacuolar border has been constructed and is reconstructed again by a polar arrangement of molecule groups, at the borderline of the protoplasma and the liquid inside the vacuole. It is quite comprehensible that the polar groups of the long molecules of fatty acids tend to give remarkable sharp and clear borderlines. In fig. 6 such small vacuoles are demonstrated in a lysol membrane, treated with acetic acid and partially dehydrated again by the addition of ammonia. The same concentration of particles may be observed at the surface layer of the entire membrane (fig. 1 and 6). The large surface activity of these hydrophile colloids in this way gives origin to solid border layers, which in the same

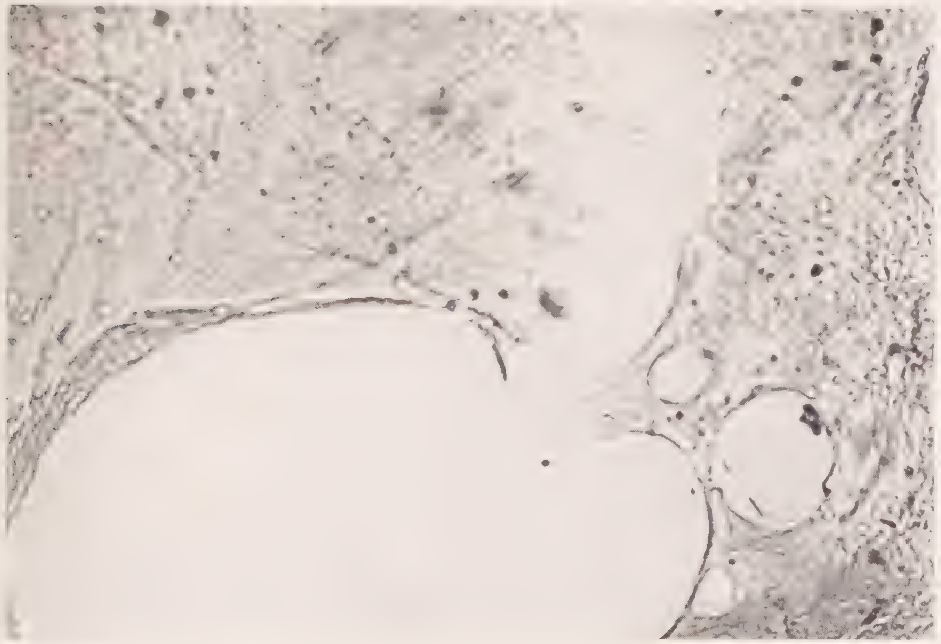

Fig. 6. Part of a membrane treated with 0.1 procent acetic acid, and afterwards with ammonia. Concentration of particles in the borderline of large and small vacuoles. × 560.

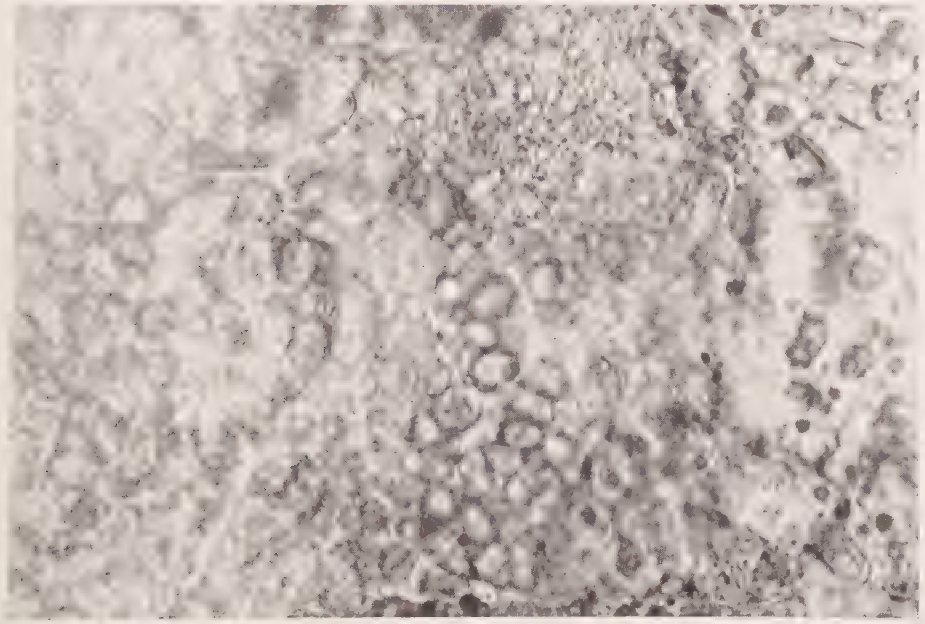

Fig. 8. Scattered pseudonuclei in a membrane from a lysol solution. × 480.

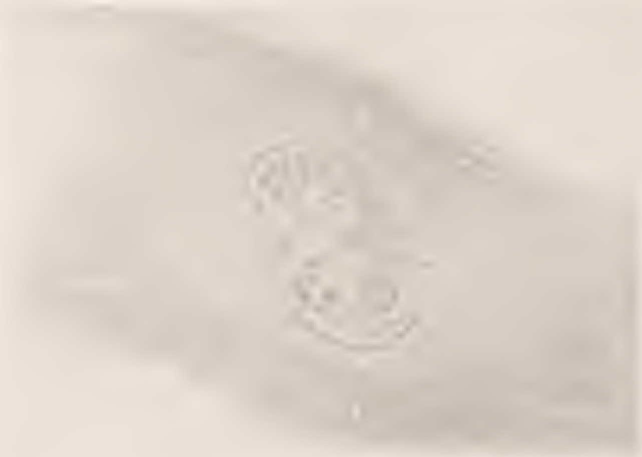

Fig. 7. Pseudonucleus in the midst of fibrillae, formed spontaneously in a lysol solution. (× 1300).

Fig. 9. Myeline (mesomorphic) corpuscles with radiation in a soap-gel. Pseudonuclei in the centre. (× 560).

way may be observed in living tissues, e.g. the reconstruction of the membrane of the nucleus after division, the formation of the egg. membrane a.s.o. Like a surface film immediately surrounds cut off particles of the living cell, the large globules, sometimes stringed off from the viscous lysol membrane, show in darkfield illumination sharply defined borderlines, due to the polar grouping of the molecules.

The fibrillae of these membranes are anisotrope. When acetic acid has been added, there remains in the beginning a diffuse lighted field between crossed nichols, even when the regular lines of the fibrillae have disappeared. However, when the hydration increases, and the borders of the membranes have grown out to slender projections and bridges, like described above — then in these parts devoid of visible particles, anisotropy is no longer observed, except in the borderlines. As soon as ammonia has been added, anisotropy may return at the spots where fibrillae tend to be reconstructed.

It seems probable that the here described membranes own their origin in this polyphasic colloid system, to a dehydration of soap by the cresolum of the mixture. The commercial lysol exists of a mixture of potassium soap and crude cresolum, in equal portions, the latter substance being principally a mixture of meta — and para —, with a small quantity of ortho cresolum. The fibrillary system of the membranes resembles indeed a soap curd, though it is less soluble in water and more resistant to high temperature than the latter one. In trying to solve pure cresolum in natrium oleate (Marseille soap), I did n't succeed in obtaining any membranes.

Probably at the phase limit of the polyphasic system soap-cresolum, the concentration of the soap micellae increases, as a consequence of the large surface tension of the soap, into which the cresolum has been solved. This increase of concentration may cause a state of oversaturation. In this state — due to the special structure of the soap molecules, aniso-diametric particles show a tendency to arrange themselves in regular rows.

The fibrillae remain unaltered in glycerine. Also in the more homogeneous gel state after the disappearance of the fibrillae, the membranes can be kept in this medium.

By very slow evaporation (at room temperature) of a clear lysol solution, one obtains, besides the membranes, a lot of smaller bodies of mesomorphic character, which again resemble structures in living nature: myeline threads, which like nettle threads are thrown out of tiny capsulae, rows of slender threads bending to and fro, which resemble bacteriae, oval bodies budding like yeast cells, ribbonlike threads and finer ones, pencillike splitting at the poles. Special attention is drawn by structures, which also at high power (× 720 and higher) perfectly resemble nuclei of living cells, where even, like one sees in fig. 7 (plate II) the nucleolus is not absent. Fig. 8 (plate II) gives a survey of such structures. They often appear concentrated in strands, while other parts are quite devoid of them. Even in dimension these bodies resemble nuclei.

When not suspecting the origin, the histologist does not hesitate to describe them as such in the microscopic field. There is such a degree of resemblance, that in the beginning I suspected an infection with animal material, till in samples of lysol, filtered before use, the same bodies appeared again. Moreover sometimes (though rarely), comparable structures may appear in gels of natrium oleate (Marseille soap), as one sees from fig. 9 (plate III). They are found there in the midst of the local accumulation of small myeline corpuscules, which, surrounded by a radiation of mesomorphic threads, already appear in concentrations of soap, before the "curd" stage has been reached.

In relation to these nuclear bodies, I wish to mention the appearance of other comparable structures, arising by the fusion of small vesicles, which on their part arise from mesomorphic (myeline) threads. This construction reminds of the reconstruction of the living nucleus from karyomeres, that is in last instance from threadlike bodies, the chromosomes. These pictures are comparable with those given by K. BELÄR ("Die cytologischen Grundlagen der Vererbung", fig. 42 d. and e., p. 56) representing the karyomeres of the Axolotl. Only homologies, which however demonstrate how life is bound to forms, which also are represented elsewhere in the microcosmos of more elementary substances.

In the here described slowly evaporated solution of 0.5 procent lysol, the structures may change from week to week, depending of the concentration and the temperature. Sometimes there exists a tendency to form fibrous membranes, sometimes in an oversaturated state brought at higher temperature, bundles of soap crystals are formed, which disturb the abovenamed homologies with living elements.

Also by mechanical influence the fibrillae of the membrane may disappear. Pressure on the coverglass changes fibrous bundles often into a homogeneous looking mass, without however producing the hydrated viscous elastic membranes which are obtained by the action of acetic acid. This disturbed fibrillary structure points to an easily caused rupture of the polar arrangements of the anisotrope particles, either by alteration of electric charge, either by mechanic influence. As mechanic pression may cause fibrillae to disappear, — at the other side one sometimes succeeds by application of a local needlepoint pressure, to cause an intensive local radiation in the midst of the gelatinous mass: Artificial radiations like they have already been described in 1899 by A. FISCHER [1]) under the influence of local traction in sections of elderwood, impregnated with albumen.

The fibrillae are basophil, in accordance with their positive electric charge. They may be lightly stained with methylen blue. This colour is kept by the membrane, when, after addition of acetic acid, the fibrillae have disappeared. In the midst of the basophil substance vacuoles may concentrate picric acid in a higher concentration than that of the solution offered to them. A comparable phenomenon has been recently described by W. SCARTH [1]) in dead and living plant vacuoles.

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[1]) Fixierung, Färbung und Bau des Protoplasmas. Verlag GUSTAV FISCHER Jena 1899

In an adhering paper will be described the faculty of fibrillae to adsorb silversalts. This also concerns the fibrillae in soap curds of natrium oleate (Marseille soap). When argyrophil fibrillae and argyrophil reticula are formed in organic substances of such elementary structure, histologists have to be careful in drawing conclusions from silver impregnations in animal tissues. When pieces of a soap-curd (f.i. a 10 procent natrium oleate) are put into 0.1—5 procent silver nitrate, it sometimes happens that the fibrous structure is partially solved at the surface. This may give rise to regularly alternating layers which, after silver-reduction, alternately are black and pale, the latter with suspending granules : the well known picture of the circles of LIESEGANG.

In soap curds of natrium-oleate (Marseille soap) acetic acid in low concentrations may also change the fibrous condition into a more or less viscous trabecular system with disappearance of the fibrillae. However, this condition never has the stability and resistance of the one studied in the lysol membranes. Hardly formed at the surface, the structure is immediately solved. The plastic character of the extended proliferating elastic gelatinous mass, as studied in the lysol membranes is never obtained. Gels and curds of soap in different concentrations, ranging from 0.5 till 10 procent has been used for this investigation. Quite instructive for the cytologist is the study of the soapgels, in relation to the above described well known centres of mesomorphic corpuscules, surrounded by a radiation of double bounded loops and ribbons (fig. 9). The latter often continue directly in the fibrillae of the curd. In gels of lower concentration these complicated mesomorphic structures may be found, when even with dark field illumination distinct fibres can 't yet be discovered.

As the soap get older, the number of these radiating centres increases till the gel has changed into the well known opaque fibrous curd.

In the transparent soap gel they are perceptible as small white points. Augmentation seems to happen by spontaneous genesis of numerous myeline central corpuscules (fig. 9), but also by division of existing centres : Radiation, primarly surrounding the total mass of the myeline corpuscules, is localised at the poles ; between the divided centres traction fibres arise. The whole resembles the achromatic figure of mitoses, where only the solitary centriol is represented by an endless number of small myeline corpuscules. Instead of the bipolar, sometimes tripolar or multipolar centres of division are found.

As to the electric charge of these centres, their power to adsorb basic aniline dyes, in contrast with the interlying gel and fibres, points to a positive charge. Bromthymolblue can 't be used as an indicator, because it is not adsorbed. As these soap gels have a tendency to be solved in water, the aniline dye (e.g. methyl violet) has to be added in substance to the gel.

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[1]) Protoplasma Bd. 2, 1927, p. 189.

The here described centres seem to have a slight higher resistance to high temperature than the fibres of the curd which are dissolved in a 4,5 procent soap gel at about 45°, followed by a crystallisation into irregularly spread crystals of natrium oleate. It is only above 50° that the myeline central corpuscules disappear.

The plastic multiform character of the mesomorphic membranes of the lysol solution, described in these pages, give rise to structures which have a great morphological likeness with structures, one meets every day when doing histological and cytological research. In these elementary substances these structures arrive, change and disappear in the most variable ways, under the influence of time, temperature, artificial or natural change in electric charge. Especially the behavior of these elementarely built membranes, throw new light on the permanent changes which undergoes the fibrous tissue in living organism. Studying recently an alveolar layer underneath the epithelium of the skin in the living tadpole, I had already the opportunity to make a comparison with conditions found during the study of these lysol membranes [1]). This living alveolar layer in the tadpole, a conducting field of nerves and finest cell projections, has to be considered as a border layer of mesenchym, which is not permanently bound to an identical structure. That is to say, it is subject to alterations in phase, as always is the case in fibrous tissue where fibrillae are formed and solved again.

The multiform character, shown by these elementary mesomorphic structures, is due to the electric charge of the micellae, their polar arrangement and rearrangement, also to the possibility of alternate hydration, dehydration and of hysteresis. It allows the student of these phenomena to get some insight into plastic conditions inside the complicated organism. Where mesomorphic substances in the living organism act even without any cell connections, these special conditions of the colloid state tend in alternative play to contribute to the temporary and permanent structure of the body.

Summary.

Alterations in phase, comparable with those in the living body, have been studied with the aid of thin floating membranes which are spontaneously formed in an old 0.5 procent solution of lysol. Special attention is drawn to the appearance and disappearance of fibrillae, the concentration of micellae with polar arrangement in surface borders and to the plastic multiform character of this mesomorphic material, which at every moment — even sometimes in fine details — gives rise to structures which resemble tissue and cell structures in the living organism.

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[1]) M. A. VAN HERWERDEN und L. J. AKKERINGA. Ueber die Lebendbeobachtung einer Wabenschicht im Randgebiete des Bindegewebes. Zeitschr. f. Zellf. und Mikr. Anat Bd. 7, 1928, S. 33.

Histology. — *Argyrophil nets and fibres outside the Organism.* By M. A. VAN HERWERDEN. (Communicated by Prof. J. BOEKE.)

(Communicated at the meeting of January 25, 1930)

In a former article [1]) I described the behavior of membranes, formed in a 0.5 procent solution of commercial lysol, which spontaneously and under the influence of different agents, gives rise to structures, the histologist and the cytologist are familiar with. During this investigation a number of experiments have been made on the faculty of staining of these structures. It appeared i.m. that the fibrillae in membranes, formed spontaneously in the lysol, have a great affinity for silver. As the silvernitrate, which has been used in a 0.5—5 procent solution, may frequently solve the peripherical layer of fibrillae before congulation sets in, other structures than fibrillae may also be obtained. In this way bundles of black fibrillae and a fine black reticulum are frequently found side by side.

Technique : The thin floating membranes have been rinsed in aq. dest. and placed during 20—30 minutes into a 0.5—5 procent solution of silvernitrate in the dark. After this they are put back into aq. dest. and exposed to sunlight. With gold impregnation (1 procent natrium aureate) the same method has been followed. In this latter case, 5 drops of a 1 procent acetic acid solution pro 5 cm^3. has been added to the aq. dest.

As a result of this treatment, the tiny membranes loose their elasticity. They grow bristle and generally undergo spontaneous fragmentation. Pieces of these fragments are examined in glycerine after being covered with a cover slip. Where the blackness is not too intense, one sees fine bundles of black fibrillae and a reticular structure which completely resembles argyrophil fibres and reticula (fig. 1), like they are described in the embryo before the appearance of collagene fibres, and in the tissues of many organs of the adult.

These argyrophil structures which even in certain spots show elements resembling neuroglia cells (fig. 2) and nerve fibres, are most suggestive. The histologist, without former information about the origin of the preparation, would take these argyrophil structures from lysol solution, for real tissue elements. Also in gels of natrium oleate (Marseille soap) one sometimes succeeds in obtaining such silver impregnations of fibrillae and other elements (fig. 3).

In histology the question, as to the origin and formation of argyrophil fibrillae and reticula in the living organism, remains of great interest. In how far do tissue cells contribute to this origin? What relation do the argyrophil fibres have to collagene fibres? The material here described, demonstrates that very simple mesomorphic substances with polar arrangement of particles are able to show argyrophil fibrillae and reticula, like they appear after silver impregnation in the living organism. It therefore is quite possible that such colloidal structures may arise in the living organism, without any direct influence of cell protoplasm. The same conclusion has been recently made by MAXIMOW in his last investigation published after his death by BLOOM [1]), relating to the argyrophil substance in tissue cultures of thymus and blood leucocytes. MAXIMOW also supposes that these fibres are formed in the intercellular liquid, independently of cells, as a crystallisation product of soluble substances in the surrounding medium. It is interesting to compare his figures (textfig. 7—11 and fig. 1—3, table VII), with those I obtained in lysol membranes and simple soap curds. This interpretation of MAXIMOW has been made very acceptible by the observation here described, that quite comparable pictures may be obtained by silver impregnation of elementary substances in non living tissue.

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[1]) These Proceedings Vol. **33**, **56**, 1930.

The silver impregnation of soap fibrillae and other mesomorphic structures which imitate cells and cellprojections and even nervefibres. should be a warning to be on our guard and to be critical, when interpreting silver and gold impregnations of fixed nervous tissue.

After the treatment with silver and gold salts the fragments grow very bristle. The slightest pressure on the coverglass may destruct the differentiation. Exposition to artificial light (when photographing and drawing) soon blackens the entire field. Only by exclusion from light these preparations keep several weeks in glycerine. Fixation of the silver by natrium hyposulfite is impossible, because the contact with this solution again alters the phase of the system, which leads to the disappearance of the fibrillae. Investigations in this direction are still continued.

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[1]) Zeitschr. f. mikr. anat. Forschung Bd. 17 H. 3—4 p. 623.

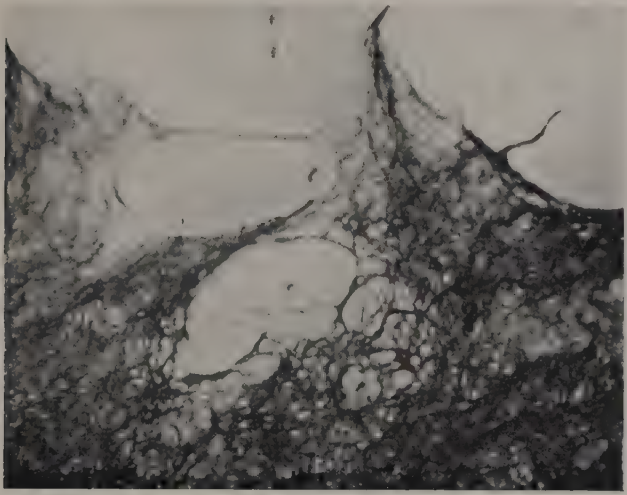

Fig. 1. Fibrous membrane from a lysol solution treated with silver nitrate. × 560.

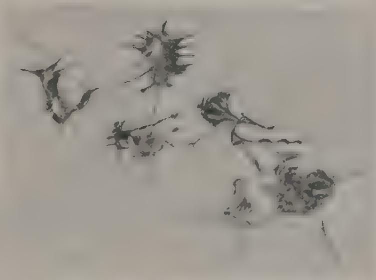

Fig. 2. Pseudocells in a soap curd treated with silver nitrate. ± × 1350.

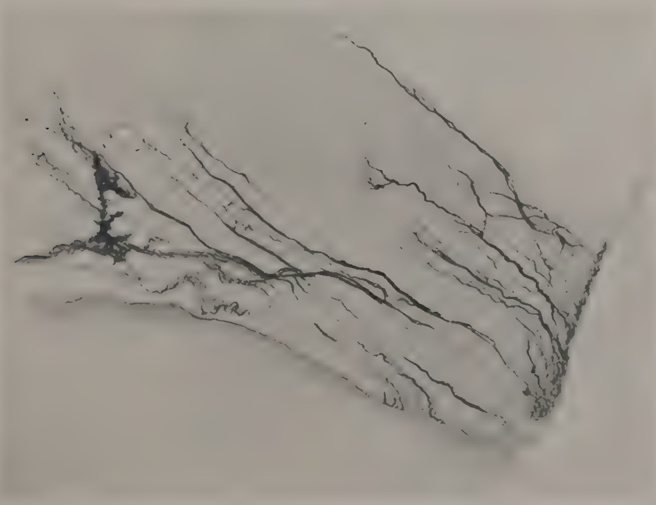

Fig. 3. Silver impregnated fibres in a 10 procent soap curd × 560.

Physics. — *Selbstabsorption in den Sonnenprotuberanzen*. Von M. MINNAERT und C. SLOB. (Mitteilung aus dem Physikalischen Institut der Universität Utrecht.) (Communicated by Prof. L. S. ORNSTEIN.)

(Communicated at the meeting of January 25, 1930).

Problemstellung.

Der Hauptzweck der vorliegenden Untersuchung ist die Bestimmung der absoluten Intensität von Protuberanzlinien, und die Vergleichung ihrer relativen Intensitäten. In dieser Abhandlung werden die Resultaten mitgeteilt von Messungen an den beiden Linien H_α und Helium λ 5876. Es wurde eine Linie des Heliums gewählt, weil dieses Gas in der Sonnenatmosphäre keine merkliche Absorption ausübt, wie sich ergibt aus dem Fehlen der Heliumlinien im gewöhnlichen Fraunhofer-Spektrum. Ausserdem ist seine Ionisationsspannung so hoch, dass nur bei extrem niedrigem Druck (etwa 10^{-16} Atm.) Ionisation auftritt. Die Intensität der Heliumlinie ist also ein gutes Mass für die Gesammtmenge der Heliumatome in der Sehrichting und für die optische Dicke der Schicht. Schon PEREPELKIN [1]) suchte durch visuelle Schätzungen näheres über diese selbe Linien zu erfahren und bekam interessante Resultate, welche weiter mit den unsrigen verglichen werden.

Messungen.

Die Aufnahmen wurden gemacht mit dem Fernrohr der Heliophysikalischen Abteilung des Physikalischen Institutes an einem Sonnenbilde von 12 cm Durchmesser; der Spektrograph hat die Littrow-Konstruktion, flaches Rowland-Gitter, 4 Meter Brennweite, Dispersion ungefähr 4 A.E. pro Millimeter in der ersten Ordnung, die für diese Untersuchung ausschliesslich benutzt wurde. Die Linien H_α und *He* 5876 konnten noch gerade auf derselben Platte aufgenommen werden.

Nachdem durch visuelle Durchmusterung des Sonnenrandes im H_α-Lichte irgend eine ziemlich hohe und helle Protuberanz gefunden war, wurde der Stand des Sonnenbildes genau bezeichnet und später immer durch elektrische Feinregulierung in Stundenwinkel innegehalten.

Dann wurden auf derselben Platte und mit derselben Expositionszeit Aufnahmen gemacht vom Protuberanzspektrum und vom Spektrum der

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[1]) E. J. PEREPELKIN, Zs. f. Phys. **49**, 295, 1928.

Sonnenmitte ; diese letzte mit einem Stufenabschwächer und mit geeignetem allgemeinen Hilfsabschwächer um eine ausgedehnte Schwärzungsskala zu bekommen, in demselben Schwärzungsgebiete wie die Protuberanzlinie.

Es stellte sich bald heraus, dass die H_α-Linie photographisch immer viel stärker war wie die Heliumlinie, so dass entweder die eine Linie zu schwarz oder die andere zu schwach wurde, was eine gute Intensitätsmessung erschwerte. Darum wurde vor den Spektrographen eine 1 cm dicke Schicht Kupfersulfatlösung eingeschaltet, deren Konzentration richtig bemessen war um beide Linien nahezu gleich stark zu erhalten. Weil das kontinuierliche Vergleichsspektrum mit derselben absorbierenden Flüssigkeit aufgenommen wurde, und alle Protuberanzlinien immer im Verhältnis zum Spektrum des Sonnenzentrums gemessen wurden, brauchte man die selektive Absorption des Kupfersulfats nicht gesondert zu bestimmen.

Immer wurden Ilford panchromatic Platten verwendet, während entwickelt wurde mit Rodinal. Die Aufnahmen wurden durchgemessen mit dem MOLL'schen Mikrophotometer, und alle Schwärzungen in Intensitäten umgerechnet nach den üblichen Methoden des Utrechter Laboratoriums. Eine Korrektion wurde eingeführt für das Himmelspektrum. Die Intensitätsverteilung innerhalb jeder Protuberanzlinie wurde gezeichnet und *die Stärke der Linie gemessen durch die integrierte Intensität, mit als Einheit die Energie innerhalb eines Angströms des benachbarten Spektrums der Sonnenmitte.* Die Zahlen für die Stärke der Linien geben also direkt „Aequivalentbreiten" an; aber die Energie der H_α-Linie ist gemessen in einer Einheit, welche energetisch nicht dieselbe ist wie die für die Heliumlinie, sondern nach den Messungen Abbots 0.83 mal so gross.

Die erste hier mitgeteilte Resultate beziehen sich auf drei Protuberanzen, deren jede in verschiedenen Höhen untersucht wurde. Die wirksame Länge des Mikrophotometerspaltes korrespondierte mit etwa 4000 à 5000 K.M. auf der Sonne, so dass ein genügendes „Höhenauflösungsvermögen" erreicht ist. Selbstverständlich sind die beobachteten Höhen nur scheinbare; die wahrscheinliche wirkliche Höhen sind berechnet nach der Methode PEREPELKIN's [1]).

Resultate.

In der Tabelle sind die Endresultate der Messungen zusammengefasst.

Die exakte Bestimmung der Intensität von Protuberanzlinien gelingt also ausgezeichnet auch ausserhalb der Finsternisse. Die absolute Zahlen der Tabelle möchten wir als Hauptergebnis unserer Arbeit bezeichnen.

Es zeigt sich, dass sie in guter Uebereinstimmung sind mit den von SCHWARZSCHILD gemessenen (Mitt. Sternw. Göttingen, **12**, 52, 1906).

Die zwei Variabelen welche die Intensitäten bestimmen sind die Höhe und die optische Schichtdicke, deren Mass die Intensität der *He*-Linie ist. Wir wollen also untersuchen in wieweit die Intensität der Wasserstofflinie von beiden Variabelen abhängt. Ausserdem ist das Verhältnis $\frac{H\alpha}{He}$ sehr wichtig, denn jede Aenderung in diesem Quotient beweist dass sich entweder das Verhältnis der beiden Gase geändert hat, oder dass Selbstabsorption anfängt eine Rolle zu spielen.

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[1]) E. J. PEREPELKIN, Zs. f. Phys. **49**, 299, 1928.

Die Abhängigkeit des Verhältnisses H_α/He von He-Intensität und Höhe wurde untersucht nach den Methoden der Korrelationsrechnung für drei veränderliche Grössen 1). Aus einer vorläufigen Schätzung ergab sich, dass

TABELLE.

Intensitäten (= Aequivalentbreiten) der Protuberanzlinien H_α und *He* 5876.

N⁰.	Scheinbare Höhe	Wahrsch. Höhe	Intens. H_α	Intens. *He* 5876	Verhältn. $H\alpha/He$
I	11.500 KM.	20.500	8.4×10^{-2}	0.25×10^{-2}	33.6
	15.000	24.000	9.3	0.24	39.0
	17.500	26.500	9.7	0.31	31.8
	20.500	29.500	8.9	0.26	34.2
	23.000	32.000	7.2	0.13	56.0
II	17.000 KM.	27.000	16.2×10^{-2}	0.66×10^{-2}	24.4
	20.000	30.000	18.4	0.86	21.4
	23.000	33.000	19.4	0.87	22.4
	26.000	36.000	17.1	0.73	23.2
	29.000	39.000	12.9	0.37	35.2
	32.000	42.000	10.6	0.26	40.1
	34.000	44.000	9.1	0.21	44.3
III	4.500 KM.	13.500	4.29×10^{-2}	0.30×10^{-2}	14.3
	8.500	17.500	3.88	0.41	9.5
	11.100	20.100	5.30	1.06	5.0
	14.800	23.800	7.12	1.79	4.0
	16.900	25.900	5.14	1.05	4.9
	22.400	31.400	3.08	0.50	6.2

$\log \frac{H\alpha}{He}$ eine nahezu lineare Funktion ist von *log He*-Intensität und von

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1) Sehe z. B.: A. PÜTTER, Die Auswertung zahlenmässiger Beobachtungen in der Biologie. Hptst. III. — F. ZERNIKE, Hdbuch der Physik, Bd. III, 487, 1928.

der Höhe. Nennen wir diese drei Veränderlichen bzw. 1, 2, 3. Man findet dann die drei totale Korrelationskoeffizienten :

	I	II	III
$r_{12} =$	-0.79	-0.84	-0.81
$r_{13} =$	$+0.48$	$+0.75$	-0.57
$r_{23} =$	-0.47	-0.71	$+0.34$

Diese Zahlen beweisen noch nicht, dass *Ha/He* wirklich korreliert ist sowohl mit der Höhe als mit der Heliumintensität. Es könnte ja sein dass die Korrelation mit der Höhe z.B. nur eine scheinbare ist, weil Höhe und *He*-Intensität selbst untereinander korreliert sind. Die richtige Beziehungen erhält man aus der Berechnung der partiellen Korrelationskoeffizienten zwischen zwei der Veränderlichen, bei konstant gehaltener dritten. Man findet :

	I	II	III
$r_{12.3} =$	-0.66 ± 0.21	-0.73 ± 0.19	-0.80 ± 0.15
$r_{13.2} =$	$+0.40 \pm 0.32$	-0.02 ± 0.40	-0.53 ± 0.30
$r_{23.1} =$	-0.22 ± 0.36	$+0.02 \pm 0.40$	-0.25 ± 0.38

Das Ergebnis ist nicht zweifelhaft : *das Verhältnis H_α/He ist deutlich abhängig von der He-Intensität, und zwar nimmt es ab mit zunehmender He-Intensität.* Die Korrelation mit der Höhe dagegen ist unmerkbar, oder (für die Protuberanzen I und III) kaum reell.

Man erhält eine leidliche Darstellung unserer Ergebnisse durch die Formeln :

$$H_\alpha = 0.81\, He^{0.37} \;\dots\dots\dots \qquad \text{(I)}$$

$$H_\alpha = 1.53\, He^{0.45} \;\dots\dots\dots \qquad \text{(II}$$

$$H_\alpha = 0.31\, He^{0.37} \;\dots\dots\dots \qquad \text{(III)}$$

wo die Intensitäten H_α und He gleich in Aequivalentbreiten gemessen sind (Sehe Fig. 1 und 2).

Eine ähnliche Abhängigkeit von der *He*-Intensität wurde auch durch Perepelkin gefunden, aber *viel* weniger ausgesprochen. Seine Schätzungen sind insofern nicht direkt vergleichbar mit den unsrigen, dass er die Zahlen für 29 Protuberanzen alle zusammen verarbeitet hat, weil wir die Ergebnisse für jede Protuberanz gesondert untersuchen. Die Abhängigkeit von der Höhe welche Perepelkin findet, ist in unserem Material nicht anweisbar.

Diskussion.

Zur Vereinfachung wollen wir annehmen, dass das Verhältnis der Zahl *He*- und *H*-atomen in allen Teilen der Protuberanz dasselbe ist.

Nun gibt es drei Ursachen welche eine mögliche Korrelation zwischen dem Verhältnisse H_α/He und der He-Intensität ergeben:

1⁰. Die Ionisation;
2⁰. Die Auslöschung des Resonanzlichtes durch Stösse;
3⁰. Die Selbstabsorption.

1⁰. Die Intensität der He-Linie, also die Zahl der He-Atome in der Sehrichtung, wird ein rohes Mass sein für den Druck in der Protuberanz; während das Verhältnis H_α/He dem nicht ionisierten Bruchteil H-atomen proportional sein wird.

In diesem Falle ist nach *Saha*:

$$\frac{x^2}{1-x^2} \sim \frac{1}{p}$$

wo $x =$ ionisiertes Bruchteil, $p =$ Druck. Die Abhängigkeit der Grösse $1-x$ von p ist dargestellt durch Fig. 3. Ein Vergleich mit den Beobachtungen (Fig. 1) zeigt keine Spur von Aehnlichkeit. Während also die Abhängigkeit von der Höhe durch PEREPELKIN an Ionisation zugeschrieben wird, ist die Abhängigkeit von der He-Intensität sicher durch eine andere Ursache zu erklären.

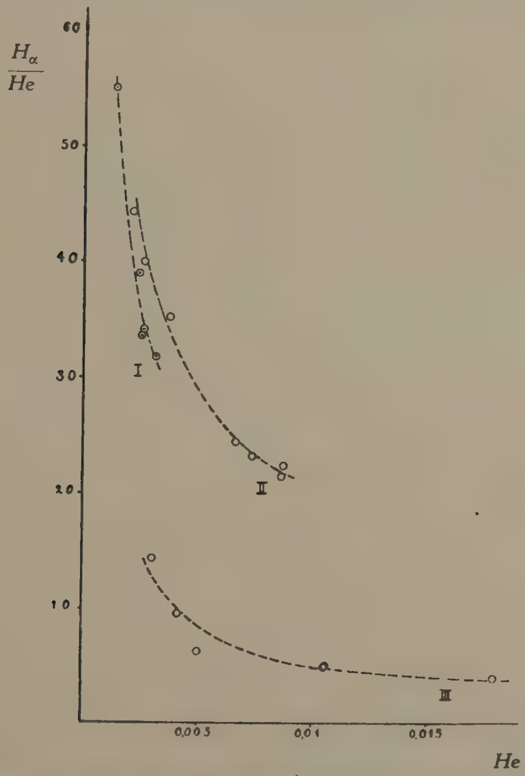

Fig. 1. Aenderung des Verhältnisses H_α/He mit der Schichtdicke.

2°. Es könnte sein dass ein Bruchteil der angeregten *He*-Atome durch Stösse mit Wasserstoffatomen im Normalzustande strahlungslos zurückkehrt. Abgesehen von der Unwahrscheinlichkeit, dass Stösse eine wichtige Rolle spielen bei so geringer Dichte, wie sie in Protuberanzen herrscht, zeigt man leicht, dass bei dieser Hypothese die Intensität der Heliumlinie bei zunehmender Wasserstoffintensität immer langsamer anwachsen muss. Die Beobachtungen ergeben den Gegenteil. (Fig. 1 : bei wachsender *He*-Intensität, also auch bei wachsender *H* -Intensität, wird die *He*-Linie relativ stärker.)

3°. Die Selbstabsorption, welche zu vernachlässigen ist bei der *He*-Linie, wird für die H_α-Linie ein immer langsamer anwachsen der Intensität verursachen bei zunehmender Schichtdicke, was schon qualitativ zutreffend erscheint.

Eine quantitative Abschätzung erhalten wir nach der Methode A. PANNEKOEK's 1). Es wird angenommen dass die Spektrallinie nur durch Doppler-Effekt verbreitert ist. Die Intensität, mit dem Einfluss der Selbst-

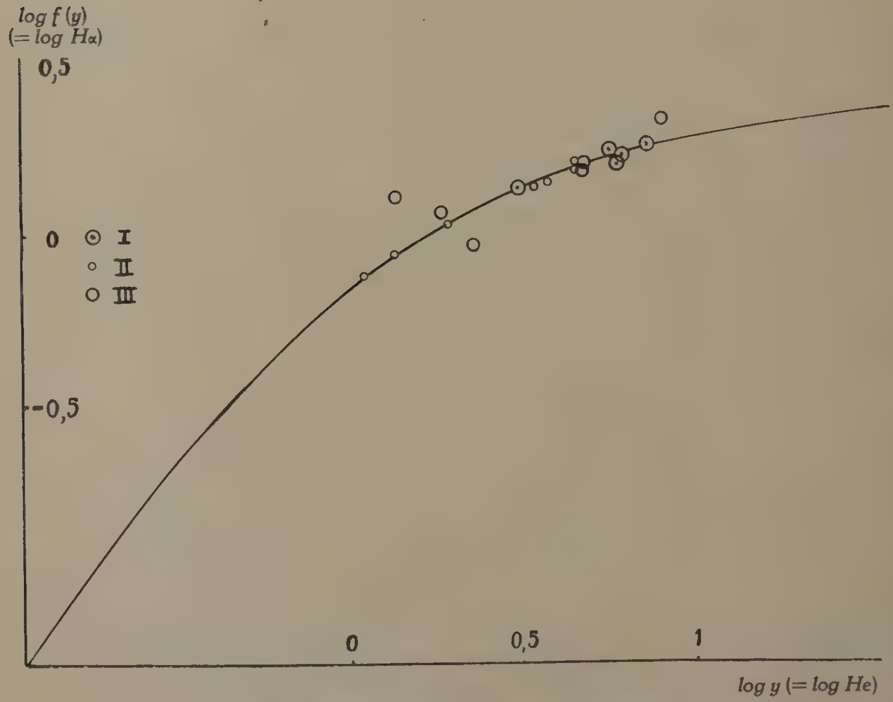

Fig. 2. Selbstumkehr in der Protuberanzlinie H_α.

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1) Bulletin Astron. Instit. of the Netherlands IV, N°. 158, S. 263, 1928.

absorption, wird für jede Wellenlänge gesondert berechnet und über die ganze Linie integriert. Man findet

$$i = Pb \int_{-\infty}^{\infty} \left(1 - e^{-y e^{-\pi u^2}}\right) du,$$

wenn $y = x \varrho l$ die halbe optische Dicke der Protuberanz bezeichnet, $e^{-\pi u^2}$ die Verbreiterung der Linie durch die Wärmebewegung, P die Plancksche Funktion, b die mittlere Linienbreite. Das Integral, welches Pannekoek $f(y)$ nennt, wurde durch mechanische Integration berechnet und in Fig. 2 auf doppelt logarithmischer Skala gezeichnet. In derselben Figur sind die Beobachtungspunkte der drei Protuberanzen durch Translation nach beiden Koordinaten mit der theoretischen Kurve zur Deckung gebracht.

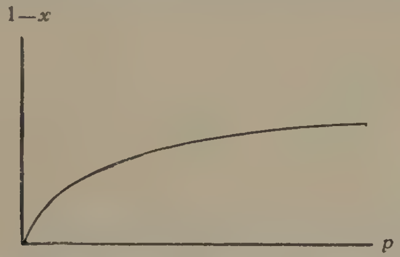

Fig. 3. **Prozent nicht ionisierte Atome als Funktion des Druckes.**

Die Uebereinstimmung ist genügend. Es ergibt sich also, dass die Intensität der *Hα*-Linie in Protuberanzen sehr merkbar beeinflusst ist durch Selbstabsorption; ohne diesen Effekt würde die Intensität der Linie je nach den Fällen 1 bis 8 mal so stark sein wie jetzt beobachtet wird.

In einer späteren Veröffentlichung hoffen wir über weitere Messungen zu berichten und aus den numerischen Werten weitere Schlüsse zu ziehen.

Herrn Professor Dr. L. S. Ornstein danken wir herzlich für das Interesse das er dieser Arbeit entgegenbrachte.

Anmerkung bei der Korrektur. — Eine vierte Protuberanz, auf derselben Weise untersucht, ergab eine fast völlige Uebereinstimmung mit Protuberanz III.

Physics. — *Isotherms of CO_2 between* 0° *and* 100° *C.* By G. P. NIJHOFF, A. J. J. GERVER S.J., and A. MICHELS. (Communication N⁰. 26 of the VAN DER WAALS-*Fund.*) (Communicated by Prof. J. D. VAN DER WAALS Jr.)

(Communicated at the meeting of January 25, 1930).

The isotherms communicated in this paper were measured by the method already described by MICHELS and GIBSON [1]). The work was undertaken in order to compare the results obtained by this method with those of AMAGAT [2]) at high pressures, and also to investigate the possibility of using the contact method for the region in which gas and liquid coexist. As AMAGAT did not publish data for this gas above 1000 atm. and as we wished to have some preliminary figures for higher densities, we took the opportunity of measuring a few points in the higher region up to 2000 atm.

Considering that AMAGAT did not claim a greater reproducibility than 1 in 1000, and that the absolute accuracy of his pressure measurement above 400 atm. is unknown, we may say that the agreement of our values is very satisfactory. At lower pressures our values are in agreement with the more accurate data given by KEESOM [3]).

During the measurements of the coexisting phases some technical difficulties were encountered, but it was possible to overcome these. As the pressure in this region was not a function of the volume, we can conclude that the gas used, which was purified by repeated sublimation of solid CO_2, was very pure. The difference between measurements in this region and points lying in the single phase state is the following : in the single phase state the smallest rise of the mercury column is counterbalanced by an increase of pressure. In the two phase state it is not so easy to get an exact equilibrium, as the platinum points are fused in the narrowest part of the tube and the capillary is changing rapidly.

At the same time the latent heat produced by the condensation disturbs the temperature equilibrium. a disadvantage that cannot be decreased by stirring.

This results in the pressure measurements not being so reproducible as in the single phase state.

It is not possible to give the absolute accuracy of the higher points, as the calibration of the pressure balance for the higher pressures has not yet been completed.

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[1]) A. MICHELS and R. O. GIBSON, Comm. of the VAN DER WAALS-Fund N⁰. 24, Ann. der Phys. **87**, 850, 1928.

[2]) E. H. AMAGAT, Ann. de chim. et de phys. (4), **29**, 246, 1873.

[3]) W. H. KEESOM, These Proc. **12**, 616, 1903. Leiden Comm. N⁰. 88, Thesis Amsterdam.

	d_A	p	pv_A		d_A	p	pv_A
100°50 C.	76.159	83.295	1.0937	39°47 C.	76.295	59.355	0.7780
	155.992	141.116	0.9046		156.256	80.571	0.5156
	239.46	195.82	0.8178		239.84	87.471	0.3647
	355.74	335.23	0.9423		356.22	112.18	0.3149
	420.95	522.89	1.2422		421.39	187.23	0.4443
	493.04	955.22	1.9374		493.36	440.82	0.8935
	582.96	(2164.7)	(3.713)		582.91	1320.9	2.266
79°50	76.208	75.202	0.9868	20°94	76.332	51.518	0.6749
	156.088	120.702	0.7733		156.327	57.75	0.3694
	239.60	158.19	0.6603		239.94	57.73	0.2406
	355.92	256.98	0.7220		356.35	57.82	0.1623
	421.11	406.46	0.9652		421.51	86.878	0.2061
	493.16	778.82	1.5792		493.42	280.66	0.5688
	582.96	1870.2	3.208		582.85	1056.3	1.813
57°90	76.256	66.766	0.8755	0°	76.370	34.38	0.4502
	156.181	99.490	0.6370		421.69	34.37	0.08151
	239.73	119.90	0.5001		493.49	99.460	0.20155
	356.08	178.13	0.5002		582.75	746.81	1.2815
	421.27	287.95	0.6835		649.41	1934.5	2.979
	493.28	597.19	1.2107				
	582.94	1576.7	2.705				

Chemistry. — *Innere Gleichgewichte in den festen Phasen I* Von A. SMITS. (Communicated by Prof. P. ZEEMAN.)

(Communicated at the meeting of January 25, 1930).

1. Stellt man eine gewisse Eigenschaft als Funktion der Temperatur dar, so meinte BENEDICKS im Jahre 1912, ohne mit der Theorie der Allotropie bekannt zu sein, vier „Types of Allotropy" aufstellen zu können, welche in Fig. 1 wiedergegeben sind.

BENEDICKS meinte, dass der Typus 2 vorkommen wird, wenn vor Erreichung des Umwandlungspunktes sich eine feste Lösung der zweiten Modifikation, welche bei höherer Temperatur stabil ist, in der ersten bildet. Beim Typus 3 wurde sich dagegen oberhalb des Umwandlungspunktes eine feste Lösung von der ersten in der zweiten Modifikation bilden. Typus 4 stellt eine Kombination von 2 und 3 dar, und bei Typus 5 ist der Umwandlungspunkt verschwunden, und es besteht nur ein kontinuierlicher Uebergang zwischen den an der ersten b.z.w. zweiten Modifikation reicheren festen Lösungen.

Verfasser zeigte schon in der Theorie der Allotropie Seite 16, dass diese verschiedenen „Types of Allotropy" [1]), von BENEDICKS sofort aus der Theorie der Allotropie abgeleitet werden können, jedoch muss dabei mit *Nachdruck darauf hingewiesen werden, dass nach dieser Theorie der eigentümliche Verlauf der Linie ab in Typus 2 dadurch erklärt werden muss, dass vor Erreichung des Umwandlungspunktes eine deutliche Verschiebung des inneren Gleichgewichts eintritt, wobei die Konzentration derjenigen Molekülart wächst, an welcher die zweite Modifikation reicher ist als die erste.*

Es ist aber unrichtig zu sagen, wie BENEDICKS tut, dass sich hier eine Lösung der zweiten Modifikation in der ersten bildet, denn, wennn dieses der Fall wäre, so würde die feste Lösung eine binäre Mischkristallphase sein, während wir hier eben mit Erscheinungen zu tun haben, die beim unären Verhalten auftreten. Daraus lässt sich schliessen, dass hier eine Verschiebung des *inneren Gleichgewichts* zwischen verschiedenen *Molekülarten* im festen Zustande vorliegen muss.

Es sei hier daran erinnert, dass die Theorie der Allotropie alle möglichen Unterschiede von den groberen, wie bei polymeren Pseudo-Komponenten, bis zu den feinsten, welche bei Molekülen und Atomen vorkommen können, umfasst [2]).

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[1]) Journ. of the Iron and Steel Institute **2**, 242 (1912).

[2]) Siehe „Theorie der Allotropie" Seite 2 und Proceedings Kon. Akad. Amsterdam, **32**, 603, 951, 1118 (1929).

In Fig. 2 sind die „Types of Allotropy" von Benedicks im Lichte der Theorie der Allotropie betrachtet, indem von der Pseudo-T, X-figur nur

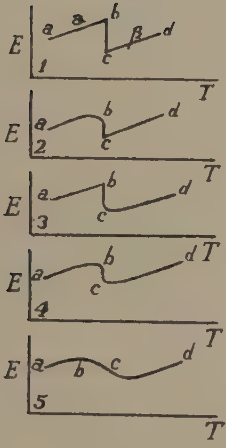

Fig. 1.

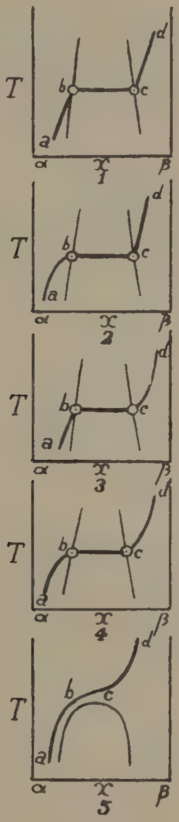

Fig. 2.

der untere Teil, d.h. das Entmischungsgebiet des festen Zustandes, gezeichnet worden ist. Der Typus 1, Fig. 2, stimmt mit Typus 1 von Benedicks, Fig. 1, überein.

Die Typen 2, 3 und 4 Fig. 1 treten auf wenn, wie die Typen 2, 3 und 4 in Fig. 2 zeigen, die inneren Gleichgewichte in einer der beiden festen Modifikationen oder in beiden in der Umgebung des Umwandlungspunktes sich stark mit der Temperatur ändern.

Es leuchtet nämlich ein, dass jede Temperaturfunktion, die von der inneren Zusammensetzung abhängig ist, einen ähnlichen Verlauf zeigen wird, wie die Linie des inneren Gleichgewichts.

Der Typus 5 von Fig. 1, wird, wie Typus 5 von Fig. 2 zeigt, vorkommen können, wenn die Kurve des inneren Gleichgewichts durch das Gebiet einer kontinuierlichen Mischungsreihe läuft, und eine starke Verschiebung des inneren Gleichgewichts stattfindet.

Verfasser hat diese kurze Auseinandersetzung aus seinem Buch wiederholt, weil in den hier folgenden Betrachtungen daran angeknüpft werden muss.

2. Aus diesen Betrachtungen geht hervor, dass, wenn, wie Verfasser schon in der Theorie der Allotropie Seite 271 bemerkte, eine abnorm starke kontinue Aenderung einer Temperaturfunktion, wie z.B. die spezifische Wärme, gefunden wird, darin eine Anweisung für die Komplexität gelegen ist.

Zur Erläuterung sei nun darauf hingewiesen, dass, wenn die innere Gleichgewichtsverschiebung mit der Temperatur sehr gleichmässig oder sehr gering ist, die spezifische Wärme, als Funktion der Temperatur, für den Fall ein Umwandlungspunkt auftritt, wie in der Fig. 3 oder 3a dargestellt werden kann.

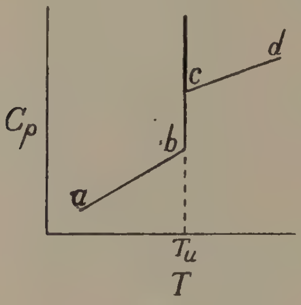

Fig. 3.

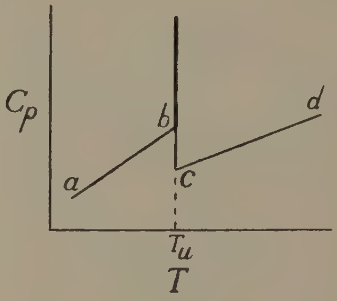

Fig. 3a.

T_u gibt hier die Umwandlungstemperatur an wo der Wert $\frac{dQ}{dT}$ plötzlich unendlich gross wird. Ich preferiere hier von dem Wert $\frac{dQ}{dT}$ zu reden, weil man nach der gebräuchlichen Definition im Umwandlungspunkt nicht von einer spezifischen Wärme reden kann.

Es ist einleuchtend, dass, wenn man untersuchen will, ob die spezifische Wärme *unterhalb* oder *oberhalb* des Umwandlungspunktes einen besondern Verlauf zeigt, man die Temperaturtrajekte bei der Bestimmung der spezifischen Wärme so wählen muss, dass diese Trajekte *niemals* die Umwandlungstemperatur einschliessen. Es ist also notwendig, dass man sich vor den definitiven Untersuchungen über die Lage des Umwandlungspunktes orientiert.

Ferner sei noch darauf hingewiesen, dass ebenso wenig wie in einem System von zwei isomorphen Komponenten immer eine ununterbrochene Mischkristallreihe auftritt, dieses erwartet werden kann bei isomorphen Pseudo-komponenten. Darum muss es nach der Theorie der Allotropie Umwandlungspunkte geben, wobei keine Aenderung in der Krystallstruktur auftritt.

Wenn wir jetzt den Fall betrachten, dass die inneren Gleichgewichte in den beiden festen Modifikationen in der Umgebung des Umwandlungspunktes sich stark mit der Temperatur ändern, welches im Typus 4 der Fig. 2 zum Ausdruck gebracht ist, so sieht man sofort ein, dass unsere Figuren 3 und 3*a* in Fig. 4 und Fig. 4*a* übergehen.

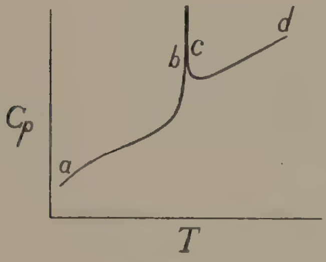

Fig. 4.

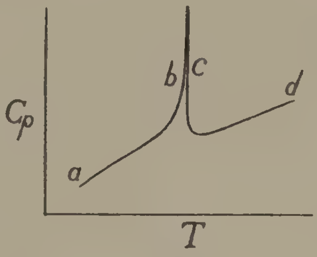

Fig. 4a.

Typus 2 und 3 der Fig. 2 wurden mit C_p, T-Figuren übereinstimmen, in welchen nur eine der zwei Kurven entweder *cd* oder *ab* einen normalen Verlauf haben.

Diese Figuren beziehen sich auf den Fall, dass es ein Umwandlungspunkt gibt. Gibt es aber kein Umwandlungspunkt und ist das einzige Eigentümliche, dass das innere Gleichgewicht sich in einem gewissen Temperaturtrajekte abnormal stark aber *kontinuierlich* mit der Temperatur verschiebt, wie in Typus 5 von Fig. 2 angegeben ist, so ist die C_p, T-Figur eine kontinuierliche Kurve mit einem Maximum wie hier unten in Fig. 5 gezeichnet worden ist.

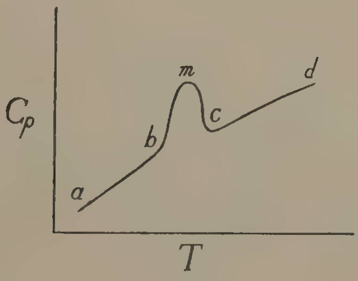

Fig. 5.

3. Es gibt nun einige rezente Untersuchungen über spezifischen Wärmen, welche so ausgeführt sind, dass die Resultate eindeutig auf eine starke Verschiebung des inneren Gleichgewichts unterhalb und oberhalb des Umwandlungspunktes hinweisen. In dieser Beziehung sei in erster Linie auf die Untersuchungen von Simon und von Simon und Simson über die spezifischen Wärme der Ammoniumhaloïden hingewiesen.

Anlass zu diesen Untersuchungen war das Studium Ewald's (Ann. d. Physik *44*, 1213, 1914) über die spezifische Wärme der Ammoniumsalze zwischen — 78° C. und 0° C. Er zeigte, dass Ammoniumchlorid, -Jodid und -Sulfat zwischen — 78° und 0° C. eine grössere mittlere spezifische Wärme besitzen als zwischen 0° und + 55° C.

Bei Ammoniumbromid und Ammoniumnitrat wurde nicht dieselbe Erscheinung gefunden, aber er meinte doch konstatieren zu können, dass der Abfall der spezifischen Wärme in diesem Gebiete —78° bis zu —0° C. schwächer war, als bei höheren Temperaturen. Weil er weiter mit dem Dilatometer keine Unstetigkeiten in Ausdehnungskoeffizienten finden konnte, meinte er, dass hier die beobachteten Erscheinungen nicht einem Umwandlungspunkt sondern einer intramolekularen Umwandlung zugeschrieben werden müssen.

Simon (Ann. d. Physik *68*, 241, 1922) bestimmte mit dem Vakuumkalorimeter die wahren spezifischen Wärmen des Ammoniumchlorids von tiefen Temperaturen an und fand bis 80° abs. eine Analogie mit Natriumchlorid. Darauf folgte bis etwa 220° abs. ein anomaler Anstieg, der zwischen 220° und 242.6° abs. noch viel stärker wurde, wie aus Fig. 6 ersichtlich ist. Dann fällt die spezifische Wärme wieder, erreicht bei ungefähr 260° einen Minimumwert und steigt dann wieder langsam an.

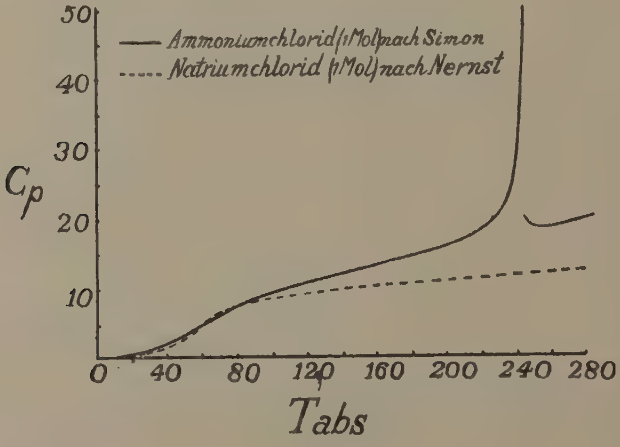

Fig. 6.

Auf die C_p-Achse ist die Molekularwärme angegeben. Simon schliesst aus diesem Verhalten des Ammoniumchlorids, dass bis zu 80° die Schwingungen innerhalb des Ammoniumradikals vollkommen abgestorben sind und das ganze Radikal wie ein Atom schwingt. Das stärkere Ansteigen der spezifischen Wärme, oberhalb 80° abs. wird nach Simon durch das Einsetzen der Schwingungen im Radikal hervorgerufen, doch bald wird dieses Ansteigen noch durch einen übernormalen Anstieg *überlagert*. Er schliesst, dass man hier mit einer Umwandlung zu tun hat, die sich auf ein grosses Temperaturintervall verteilt. Von einer eigentlichen Umwandlungstemperatur, meint er, kann man nicht reden, höchstens könnte man als solche die Temperatur bezeichnen, bei der die Umwandlung beendigt is (243°). SIMON weist in dieser Abhandlung darauf hin, dass die Möglichkeit besteht, dass viele der bekannten Umwandlungen in derselben Art, wie bei Ammoniumchlorid vor sich gehen, weil bei vielen Umwandlungen andere physikalischen Grössen, wie z.B. das Brechungsvermögen sich in derselben Art ändern, wie hier bei der spezifischen Wärme des Ammoniumchlorids gefunden ist. [MIETZEL, Z.f. Anorg. Chem. **116**, 71, (1921) und RINNE, Die Kristalle als Vorbilder feinbaulichen Wesens der Materie, Berlin (1921) S. 86.]

SIMON, SIMSON und RUHEMANN haben später (Z.f. phys. Chem. **129**, 339) nicht nur die wahren spezifischen Wärmen des Ammoniumchlorids nochmals bestimmt. sondern dabei auch die andern Ammoniumhalogeniden von etwa — 70° bis zu Zimmertemperatur in der selben Richtung studiert.

Die Resultate sind in Fig. 7 angegeben.

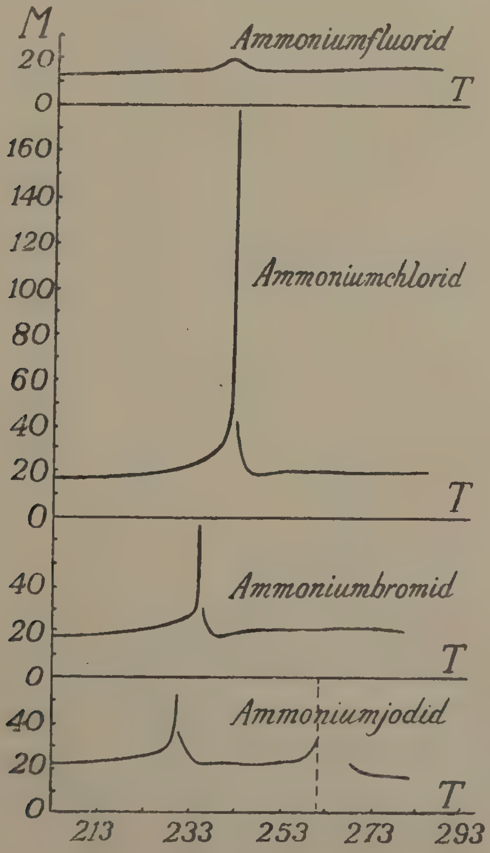

Fig. 7.

Aus den Figuren für NH_4Cl, NH_4Br und NH_4J geht also deutlich hervor, dass Maxima gefunden wurden, welche meiner Meinung nach, die Stelle angeben wo $\frac{dQ}{dT} = \infty$. Diese Stelle liegen resp. bei den Temperaturen 242.6° abs., 235° und 230.5°.

In Zusammenhang mit unseren Betrachtungen unter 2. geht hervor, dass diejenigen Bestimmungen am meisten interessant sind, welche bis dicht in der Umgebung dieser hier genannten Temperatur ausgeführt sind, aber in solcher Weise, dass die Temperaturtrajekte, über welche die spezifische Wärme gemessen wurde, niemals die mit den Maximumwerten der gefundenen spezifischen Wärmen übereinstimmenden Temperaturen enthält. Aus den gegebenen Zahlen ist nicht abzuleiten, welche Resultate auszuschalten sind, um die meist interessanten übrig zu halten, aber wenn man die hier folgenden, NH_4Cl betreffenden Tabelle von SIMON, SIMSON und RUHEMANN

NH_4Cl

T_{abs}	C_p	T_{abs}	C_p
204°	16.71	241°.7	43.10
207.4	16.81	242.5	122.52
210.3	17.06	242.6	177.36
212.8	17.54	243.2	41.72
215.7	17.92	243.9	25.44
221.3	18.70	247.0	18.76
224.4	20.05	249.7	19.60
227.5	20.49	252.4	19.80
230.4	21.56	255.0	19.78
233.5	22.51	259.3	19.74
236.2	25.40	265.0	19.55
238.8	28.38	270.7	19.55
240.8	34.90	275.6	19.60

übersieht, und man schliesst die Bestimmungen von 241.7° bis zu 243.2° aus, weil hier das gemessene Temperaturtrajekt wahrscheinlich die Temperatur 242.6° enthielt, so sieht man doch, dass hier etwas Besonders vorliegt, weil die Molekularwärme in dem Temperaturtraject 204—241° abnormal stark ansteigt, in immer rascherem Tempo, und dass von 244° bis zu 276° die Molekularwärme anfangs ziemlich stark abnimmt, um später wieder langsam anzusteigen. Dasselbe gilt auch für Ammoniumbromid und bei Ammoniumjodid wiederholt sich diese Erscheinung noch ein Mal. Man sieht sofort ein, dass dieses Verhalten darauf hinweist, dass die festen

Phasen dieser Salze komplex sind, d.h. aus verschiedenen Molekülarten bestehen, und dass das innere Gleichgewicht sich unterhalb und oberhalb des Umwandlungspunktes stark mit der Temperatur verschiebt, wie in Typus 4 Fig. 2 angegeben wurde.

Verfasser ist also mit den Auffassungen von SIMON, SIMSON und RUHEMANM, dass man hier von einem Umwandlungspunkt nicht reden kann, nicht einverstanden.

Die Maxima in der Molekularwärme geben nämlich nach Verfasser die Stelle an, wo $\frac{dQ}{dT} = \infty$. Sie geben also die Lage der Umwandlungspunkte, welche für NH_4Cl und NH_4Br bei 242.6° resp. 235° abs. liegen, während die zwei Maxima, welche bei NH_4J gefunden sind, auf zwei Umwandlungspunkte hinweisen, welche bei 230.5 und 260.5° abs. gelegen sind.

SIMON und SIMSON (Naturwissenschaften **38**, 880, 1926) fanden, dass bei NH_4Cl *keine Aenderung* der *Kristallstruktur* auftritt, aber, wie schon unter 2. gesagt ist, eine solche Aenderung auch *nicht notwendig mit dem Auftreten eines Umwandlungspunktes verbunden ist*, und man kann selbst erwarten, dass sich dieses Verhalten manchmal vortun wird.

Bei Ammoniumfluorid wurde eine C_p, T-Kurve gefunden, aus welcher, wenn sie in der Tat kontinuierlich ist, eine *vollkommen kontinuierliche* Verschiebung des inneren Gleichgewichts folgt und dieser Fall würde dann mit dem Typus 5 von Fig. 2 und mit Fig. 5 übereinstimmen [1]).

An dieser Stelle können wir noch nicht auf die Verschiedenheit zwischen den Moleküuarten, welche man hier bei den Ammoniumsalzen wird annehmen müssen, eingehen.

Die genaue Bestimmung der spezifischen Wärme, welche bei dem Ammoniumsalze solche interessanten Resultate lieferte, hat in der letzten Zeit auch in anderen Fällen ähnliche Ergebnisse gegeben. So fanden EUCKEN und KARWAT (Z.f. physik. Chem. **112**, 467, 1924) und später GIAUQUE und WIEBE (J. Amer. Chem. Soc. **50**, 2193, 1928; **51**, 1441, 1929) einen sehr interessanten Verlauf der spezifischen Wärme mit der Temperatur bei *HBr* und *HJ*, was sich aus den hier unten wiedergegebenen Figuren 8 und 9 aus der Publikation von GIAUQUE und WIEBE ergibt.

EUCKEN und KARWAT sagen in Zusammenhang mit diesen Resultaten folgendes: „Eine Schwierigkeit lag nur bei dem tieferen Umwandlungspunkte des Bromwasserstoffs und Jodwasserstoffs vor, in dem die Molwärme hier einen sehr starken bereits etwa 15° unterhalb des Umwandlungspunktes beginnenden Anstieg der Molwärmen zeigt. Die Molwärmen erreichen hier dicht unterhalb des Umwandlungspunktes recht beträchtliche Werte; ein diskontinuierlicher Einsatz der Umwandlung ist überhaupt nicht zu erkennen, sondern es scheint als ob sich die Umwandlung über ein grösseres Temperaturinterval erstreckte. Die gleiche interessante, „mit der

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[1]) Es wird vorkommen, speziell wenn die Umwandlungswärme klein ist, dass es grosse Schwierigkeiten geben wird, um zwischen den Fällen 4 und 5 zu entscheiden.

Gibbschen Phasengesetz nicht ohne weiteres vereinbare", Erscheinung wurde bereits von SIMON am NH_4Cl beobachtet und dort eingehend diskutiert."

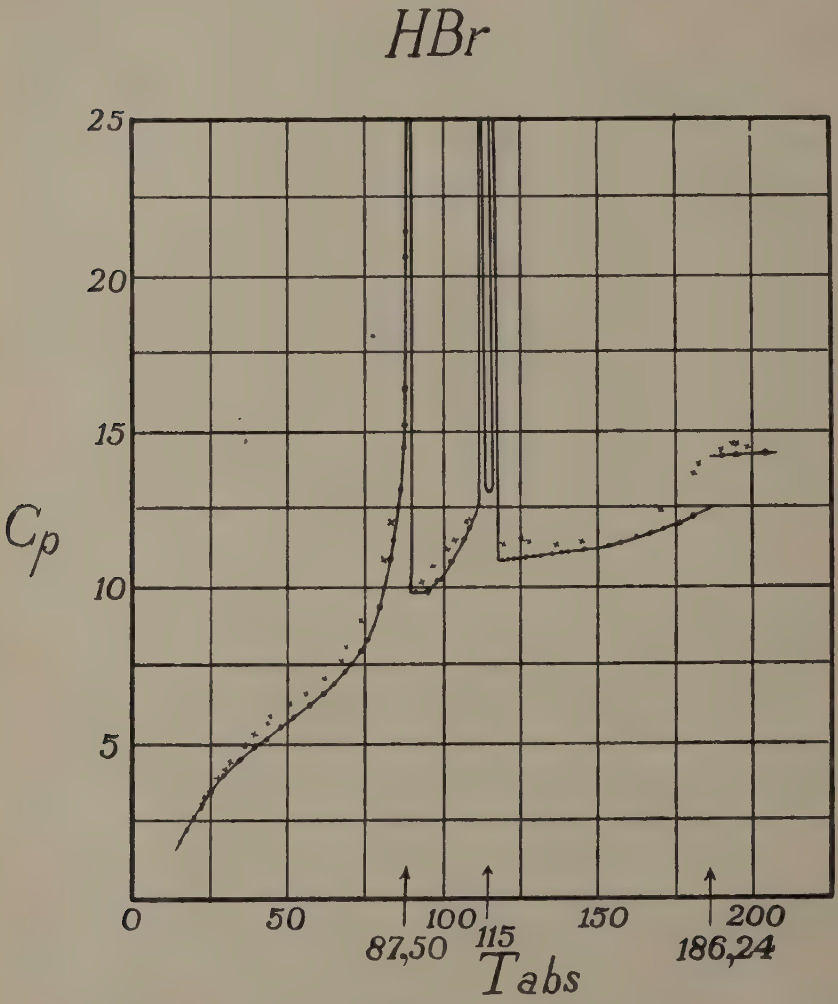

Fig. 8.

× EUCKEN und KARWAT ● GIAUQUE und WIEBE.

GIAUQUE und WIEBE schreiben: ,,The three high maxima found with *HJ* indicate gradual transitions of the type observed by SIMON in the case of ammoniumchloride".

,,It seems plausible that such transitions may be due to internal changes in the molecule structure, as has been suggested by SIMON and SIMSON".

Ob hier bei ungefähr 115° in der Tat zwei Maxima dicht hintereinander auftreten, wie GIAUQUE und WIEBE betonen, ist möglich, aber noch nicht genügend geprüft.

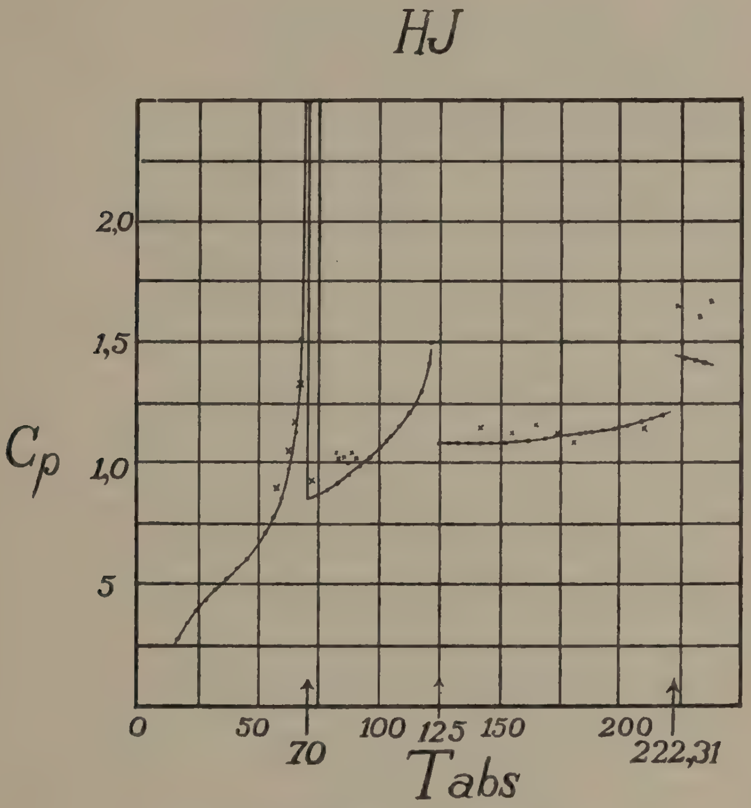

Fig. 9.

× EUCKEN und KARWAT ● GIAUQUE und WIEBE.

In Bezug auf die Resultate mit *HJ* sagen GIAUQUE und WIEBE folgendes: „The results suggest the following possibility: the transition starts as a changing thermal equilibrium between energy states of the *hydrogen iodide molecules,* both in the same crystal lattice, but when a sufficient concentration of the higher energy state has been reached, the system becomes unstable and changes to a new crystalline form".

Diese Aeusserungen, speziell diejenigen von GIAUQUE und WIEBE zeigen mit grosser Klarheit, dass sie, ohne mit der Theorie der Allotropie bekannt zu sein, eine Erklärung suchen, welche schon mittels dieser Theorie gegeben wurde.

Auch in einer vor Kurzem erschienenen Abhandlung von CLUSIUS (Z.f. phys. Chem. B 3, 41, 1929) über die spezifische Wärme kondensierter Gase werden u.m. Resultate, Methan betreffend, mitgeteilt, welche, wie sich aus unterstehender Figur 10 ergibt, den hier besprochenen Fällen vollkommen anzuschliessen scheinen.

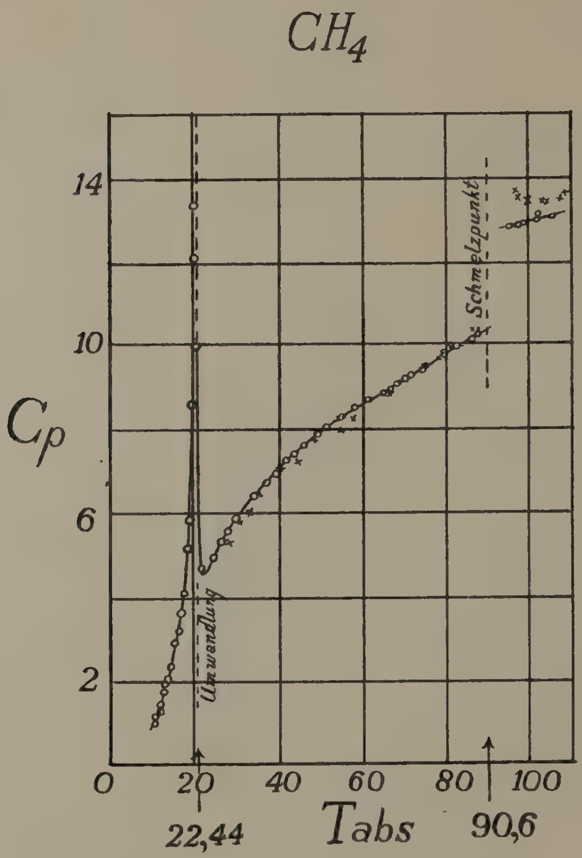

Fig. 10.
× Eucken und Karwat ‾ • Clusius.

Es ist zu bedauern, dass aus diesen Abhandlungen wieder nicht zu entnehmen ist, ob dicht unter dem Umwandlungspunkte die Temperaturtrajekte, über welche die spezifische Wärme gemessen wurde, niemals die mit dem Maximum übereinstimmende Temperatur enthielten.

Abgesehen hiervon aber ist es doch wahrscheinlich, dass auch hier sich unterhalb des Umwandlungspunktes eine ziemlich starke Verschiebung des inneren Gleichgewichts manifestiert.

Im Gegensatz zu der viel verbreiteten Meinung wird, wie ich schon bemerkte, eine Umwandlung sicherlich nicht immer mit einer Kristallstruktur-Aenderung verbunden sein, so dass aus einem Fehlen dieser Aenderung nicht geschlossen werden darf, dass ein Umwandlungspunkt nicht besteht. Das besondere, dass gefunden worden ist, liegt auch nicht im Umwandlungspunkt, sondern vor oder nach diesem Punkt, und deshalb habe ich auch absichtlich darauf hingewiesen, dass bei den definitiven Bestimmungen der spezifischen Wärmen, das Temperaturtrajekt niemals die Temperatur des Umwandlungspunktes enthalten darf.

Aus den hier betrachteten Beispielen folgt, dass das Studium der spezifischen Wärme von den festen Phasen der Ammoniumhaloiden, von HBr, HJ und von CH_4 zu dem Resultat geführt hat, dass diese festen Phasen komplex sind, d.h. aus verschiedenen Molekülarten bestehen, wobei der Ausdruck „verschiedene Molekülarten", wie schon bemerkt, [1]) möglichst breit aufgefasst werden muss.

Laboratorium für allgemeine und anorganische
Chemie der Universität.

Amsterdam, den 21. Januar 1930.

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[1]) l.c.

Chemistry. — *Untersuchung über die Komplexität des Stickstoffs.* Von A. SMITS und J. DE GRUYTER. (Communicated by Prof. J. D. VAN DER WAALS Jr.)

(Communicated at the meeting of January 25, 1930).

1. Nun es BONHOEFFER und HARTECK [1]) so wie EUCKEN und HILLER [2]) gelungen ist die Komplexität des Wasserstoffs experimentell zu beweisen und Daten zu erhalten, woraus Verfasser [3]) den Typus des Pseudo-Systems ableiten konnte, lag es auf der Hand Stickstoff zu untersuchen, um so mehr, weil mein Kollege H. A. KRAMERS mir mitteilte, dass sich auf Grund quantenmechanischer Betrachtungen erwarten lässt, dass der Stickstoff, ebenso wie der Wasserstoff, aus zwei Molekülarten zusammengestellt ist.

Während aber bei Wasserstoff die Lage des totalen inneren Gleichgewichts oberhalb 170° abs. sich beinah nicht mehr ändert, wird dieses Verhalten bei dem Stickstoff ungefähr ab 3° abs. erwartet.

Nennen wir auch hier wieder die α Molekülart den Para- und die β Molekülart den Ortho-Zustand des Stickstoffs, so wird oberhalb 3° abs. $K_{tot} = \frac{(\beta)}{(\alpha)} = 2$ sein. Der unär sich verhaltende Stickstoff wird also ein Gemisch von zwei Pseudokomponenten in innerem Gleichgewicht darstellen.

Es fragt sich nun wie rasch das innere Gleichgewicht sich einstellt Wenn dieses nicht zu schnell geht und die zwei Pseudokomponenten genug in Flüchtigkeit von einander verschieden sind, wird es möglich sein durch die Methode der fraktionnierten Destillation, wie SMITS diese schon oft bei ähnlichen Versuchen anwandte, die Komplexität zu beweisen. Wenn nämlich der Stickstoff vollkommen rein ist, und dessen ungeachtet zeigt die abdestillierte Fraktion bei derselben Temperatur einen, sei es auch vorübergehend, höheren Dampfdruck, als der Rest, so ist die Komplexität bewiesen. Nun ist die Methode der fraktionnierten Destillation eine sehr scharfe Methode zur Kontrolle der Reinheit und daher ist diese Methode zum Nachweis der Komplexität nur überzeugend, wenn die Druckdifferenz mit der Zeit oder nach Zufügung eines Katalysators schliesslich wieder vollkommen verschwindet, und also jede Fraktion am Ende denselben Dampfdruck, wie der Rest zeigt.

2. Die hier folgenden Untersuchungen bezweckten zu prüfen, ob sich die Komplexität des Stickstoffs bei der Siede-temperatur des flüssigen Stickstoffs nachweisen läszt.

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[1]) Nat. Wissenschaften **17**, 182 (1929). Z. f. phys. Chem. Abt. B **4**, 113 (1929).

[2]) Nat. Wissenschaften **17**, 182 (1929). Z. f. phys. Chem. Abt. B **4**, 142 (1929).

[3]) These Proceedings **32**, 603, 951, 1118 (1929).

Aeusserst reiner Stickstoff wurde in einem aus Jenaer Apparatenglase angefertigten Apparat, Fig. 1, bereitet. Der Stickstoff wurde in dem grossen Fraktionnierkolben *A* aus 140 gr. $NaNO_3$, 140 gr. K_2CrO_4 und 400 gr $(NH_4)_2SO_4$, unter Zufügung von 10 cc. Ammoniaklösung, in 900 cc. Wasser gelöst, durch sehr vorsichtiges Erhitzen, entwickelt.

Das Gas wurde dann sukzessiv durch drei Waschflaschen *B*, *C* und *D*; durch eine gesättigte Lösung von $K_2Cr_2O_7$ in starker Schwefelsäure im Volumverhältnis 3 : 1, dann durch zwei Waschflaschen *E* und *F* mit starker Natronlauge, sodann durch zwei Waschflaschen *G* und *H* mit starker Schwefelsäure und endlich durch eine Kondensationsflasche *I*, wie wir diese nennen, welche in ein Dewargefäss mit flüssiger Luft getaucht ist, geführt. An dieser Stelle gelangt, könnte der Stickstoff noch Spuren Stickstoffoxyd, Sauerstoff und vielleicht auch noch Spuren Wasserstoff enthalten und darum wurde er durch ein mit Kupfer beschicktes Rohr aus Supremaxglas, das sich mit Jenaer-apparatenglas verschmelzen läszt, und das in einem Fletscher-Ofen *K* mässig erhitzt wurde, geleitet.

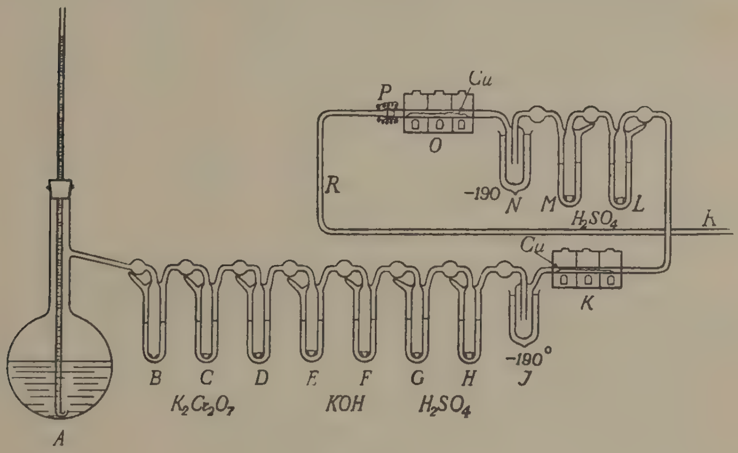

Fig. 1.

Das Experiment lehrte, dass das Kupfer an der Eintrittstelle oxydiert wurde, und das also, wenn Wasserstoff anwesend war, dieses durch die Spuren Stickstoffoxyd oder Sauerstoff überkompensiert wurde. Nach den Ofen *K* verlassen zu haben, wurde das Gas zum zweiten Male derselben Reinigung unterworfen, indem es erst wieder durch zwei Waschflaschen *M* und *L* mit konzentrierter Schwefelsäure, dann durch eine Kondensationsflasche *N*, in flüssiger Luft getaucht, und schliesslich wieder in den Ofen O. über erhitztes Kupfer geleitet wurde. Bei *P* befindet sich ein Schliff von Supremax-glas auf Jena-normal-glas, weil unser Druckapparat (Fig. 2) auch von Jena-normal-glas angefertigt war und wir Kautschuk-verbindungen umgehen wollten.

Das Rohr *R* ist an das Rohr *P* in Fig. 1 angeschmolzen. Während der Gasentwicklung war der Hahn *M* geschlossen und *N* geöffnet, wobei das Gas durch eine Waschflasche mit konzentrierter Schwefelsäure entwich und dort mit einer Phosphorpipette auf Sauerstoff untersucht wurde.

Der Druckapparat Fig. 2, ist in wesentlichem dem Apparat ähnlich, welcher SMITS in 1913 für die Untersuchungen TERWEN's anfertigen liess. Der Apparat läszt auf einfache Weise den Einfluss der fraktionnierten Destillation studieren, d.h. er stellt uns in die Lage 1^0. nach fraktionnierter Destillation, den Dampfdruck-Unterschied zwischen der abdestillierten Fraktion und den Rest zu bestimmen, und 2^0. den absoluten Dampfdruck zu messen. Nehmen wir nämlich einen Augenblick an, dass z.B. flüssiger Stickstoff von *A* nach *B* destilliert wird, dann lässt sich durch aufpressen von Quecksilber in den Schenkeln *C* und *C'* des Differentialmanometers die Dampfdruck-differenz messen.

Herrscht in *F* vakuum oder ist der Druck dort bekannt, so findet man aus der Höhe-differenz der Quecksilberoberflächen in einer der beiden Schenkeln des Differential-manometers und in dem Rohr *F* den absoluten Dampfdruck.

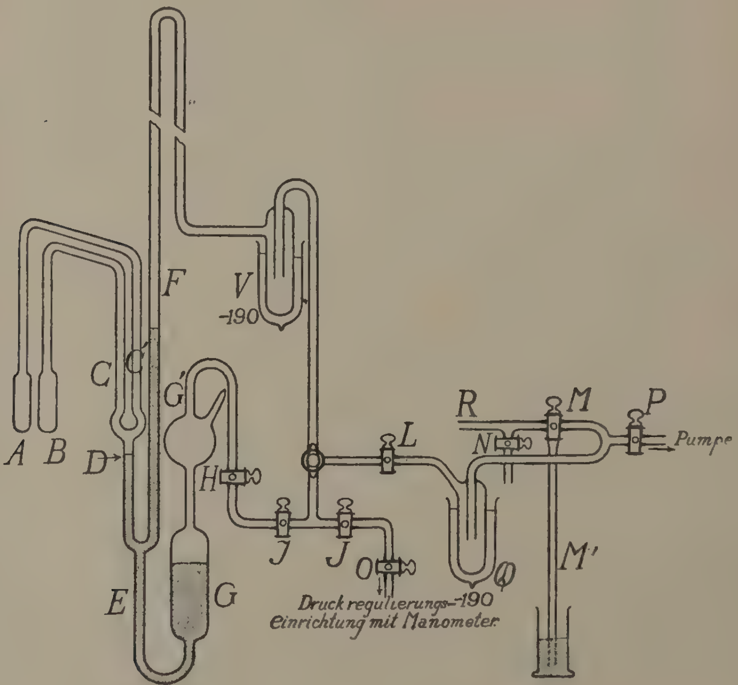

Fig. 2.

Vor der Füllung wurde der äusserst gut gereinigte Apparat, nachdem das Gefäss *G* von reinem, trocknem Quecksilber versehen war, bei geschlossenem Hahn mit Sicherheitsrohr *M*, durch *P* mittels einer Diffusion-Quecksilberpumpe evakuiert, während der Hahn *O* geschlossen aber die Hähne *H*, *I*, *J*, *L*, geöffnet und *K* so gestellt war, dass die drei Röhren kommunizierten. Das Quecksilber das jetzt in *E* und *G* gleich hoch stand, wurde einige Zeit zum sieden erhitzt, wobei die Kugel *G′* als Luftkühler fungierte.

Wenn die Luft auf diese Weise ausgetrieben war, wurde *N* geschlossen und *M* darauf vorsichtig geöffnet, wobei der ganze Apparat sich mit Stickstoffgas bis zu einem Druck ein wenig oberhalb 1 Atm. füllte, denn bei einem kleinen Ueberdruck entwich das Gas durch das in Quecksilber getauchte Sicherheitsrohr *M′*. Darauf wurde *M* wieder geschlossen, *N* und *P* geöffnet und der Apparat also wieder evakuiert, während das Gas wieder durch *N* entwich. Diese Manipulation wurde drei oder vier Mal wiederholt und dann wurde zur definitiven Füllung geschritten. Dazu wurden erst um die Kondensationsgefässe *Q* und *V* Dewargefässe mit flüssiger Luft gebracht und der Dreiweghahn *K* so gedreht, dass das Rohr nach den Hähnen *I* und *J* abgespert war. Der Hahn *O* wurde darauf mit der einen Manometer enthaltenden Druckregulierungseinrichtung verbunden, um in der Lage zu sein den Gasdruck auf die Quecksilberoberfläche in *G* so zu regulieren, dass das Quecksilber links ungefähr auf der Höhe *E* blieb, so dass der Weg durch *F* nach den Gefässen *A* und *B* frei war.

Nun stellte man um das Gefäss *A* ein Dewargefäss mit flüssigem Stickstoff, schloss Hahn *N* und öffnete vorsichtig *M*, wobei mit einem kleinen Ueberdruck erreicht werden konnte, dass ein langsamer Stickstoffstrom in *A* kondensierte. Es leuchtet ein, dass das letzte Dewar-gefäss *V* mit flüssiger Luft dazu diente, dem, übrigens äusserst reinen, Stickstoff Spuren Hahnfettdampf zu entziehen.

Nachdem Gefäss *A* ganz mit flüssigem Wasserstoff gefüllt war, wurde das Quecksilber bis zu *D* aufgepresst und dort gehalten, während zur absoluten Druckmessung der Raum oberhalb der Quecksilbersäule in *F* hoch evakuiert oder mit der Atmosphäre von bekanntem Druck in Verbindung gebracht wurde.

3. Nach verschiedenen orientierenden Versuchen wurde erst mittels des Differentialmanometers der Dampfdruck des Destillats und des Restes nach der Destillation mit der Zeit verfolgt. Dazu wurde auch um *B* ein Dewargefäss mit flüssigem Stickstoff gebracht. Liess man nun das Dewargefäss mit flüssigem Stickstoff um *A* etwas sinken, so stieg die Temperatur in *A* ein wenig, die Quecksilberoberfläche in *D* sank einige cm und der Stickstoff destillierte schnell von *A* nach *B*. Als die Hälfte des Stickstoffs überdestilliert war und die Flüssigkeitsoberflächen in *A* und *B* gleich hoch waren, dann wurde das Quecksilber rasch bis in die Schenkeln *C* und *C′* des Differentialsmanometers aufgepresst, *A* und *B* zusammen in einem grossen versilberten Dewargefäss mit flüssigem Stickstoff gestellt und der Stand der Quecksilberoberflächen in *C* und *C′* wie auch in *F* in

gewissen Zeitintervallen an der Scale mit einer Loupe abgelesen. Alle Versuche verliefen in derselben Weise und das mittlere Resultat ist in unterstehender kleiner Tabelle wiedergegeben.

Zeitdauer nach Ende der Destillation	Dampfdruck Destillat-Dampfdruck Rest in cm Hg
1′	0.10
8′	0.05
12′	0.00
120′	0.00

Man sieht hieraus, dass der Dampfdruck des Destillats nach einer Minute 1 mm. Hg. höher, als der Dampfdruck des Restes gefunden wurde und dass schon nach 12 Minuten oder vielleicht noch eher, die Dampfdrucke des Destillats und des Restes vollkommen gleich waren.

Das letzte, auf sich selbst genommen, beweist, dass es uns gelungen war den Stickstoff in *sehr reinem Zustand* zu erhalten. Der anfänglich etwas höhere Dampfdruck des Destillats kann nun eine besondere Bedeutung haben und würde darauf hinweisen können, dass es hier gelungen ist, bei der Destillation ein Destillat zu erhalten, das etwas reicher an der meist flüchtigen Pseudokomponente war als der Rest. Die Tatsache, dass diese Differenz klein ist und schnell verschwindet würde uns vermuten lassen, dass die Einstellung des inneren Gleichgewichts *ziemlich rasch* vor sich geht. Es ist dabei natürlich auch noch möglich, dass die Pseudokomponenten in Flüchtigkeit sehr wenig verschieden sind.

Nun ist es sehr schwierig über solche kleine Druckunterschiede Sicherheit zu erlangen. Es ist wahr, dass die Temperatur des Restes eben vor dem Ende der Destillation höher war, als die des Destillats ; der Dampfdruck des Restes war nämlich bei der Destillation etwa 5 cm. Hg höher, als der des Destillats, und dabei destillierten wir absichtlich so viel, dass die Flüssigkeitsoberflächen in den vollkommen ähnlichen Gefässen A und B gleich hoch waren, damit der Temperaturverlauf in der siedenden Stickstoffcolonne, welche sich in dem Dewargefäss befand, keine Fehler verursachen sollte [1]).

Wir meinten, dass dieses sehr erwünscht war, weil $\frac{dp}{dT}$ der Dampfdruckkurve in diesem Temperaturgebiet ungefähr 40 cm. Hg. und die Druckänderung per 0.001° also ungefähr 0.004 cm. Hg beträgt.

Wir haben die Versuche auch noch in der Weise geändert, dass nicht von *A* nach *B*, sondern von *B* nach *A* destilliert wurde, doch immer war das Resultat dasselbe, *immer zeigte das Destillat anfangs einen zu hohen Dampfdruck*.

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[1]) Später haben wir bemerkt, dass diese Vorsichtsmassregel nicht nötig gewesen war, denn ein Einflusz kleiner Höhedifferenzen des flüssigen Stickstoffs in A und B war nicht zu beobachten.

Es wurde bei diesen Versuchen die Temperatur des Stickstoffbades mittels eines Widerstandsthermometers kontrolliert. Aus den hier erwähnten Versuchen bekommt man den Eindruck, dass, wenn wirklich die Komplexität des Stickstoffs die beobachteten vorübergehenden Dampfdruckdifferenzen verursacht, die Einstellung des inneren Gleichgewichts mit ziemlich grosser Geschwindigkeit stattfindet.

Es schien daher lohnend den Versuch in der Weise abzuänderen, dass noch rascher der Effekt einer Destillation beobachtet werden konnte. Als der gesammte Stickstoff sich in *A* befand, wurde das Dewargefäss um *A* wieder gesenkt, während *B* tief in einem anderen Dewargefäss mit flüssigem Stickstoff stand, und mit einer Druckdifferenz von ± 15 cm. Hg möglichst schnell eine kleine Menge nach *B* destilliert, darauf wurde auch *A* wieder tief in das Dewargefäss gesenkt, wobei das Quecksilber wieder in den beiden Schenkeln des Differentialmanometers hinaufstieg, und nun wurde nicht die Dampfdruckdifferenz zwischen dem Destillate und dem Reste, sondern der absolute Druck des Destillats nach sehr kurzen Zeitintervallen gemessen.

Ehe wir das Resultat dieser Versuche mitteilen, wollen wir einen Augenblick überlegen, was erwartet werden kann, wenn tatsächlich bei sehr raschem Arbeiten ein Destillat von vorübergehend etwas geänderter Zusammensetzung erhalten wird. Die Destillation fand unter einem Ueberdruck von circa 15 cm. Hg. statt. Nach dem Hochheben des Dewargefässes

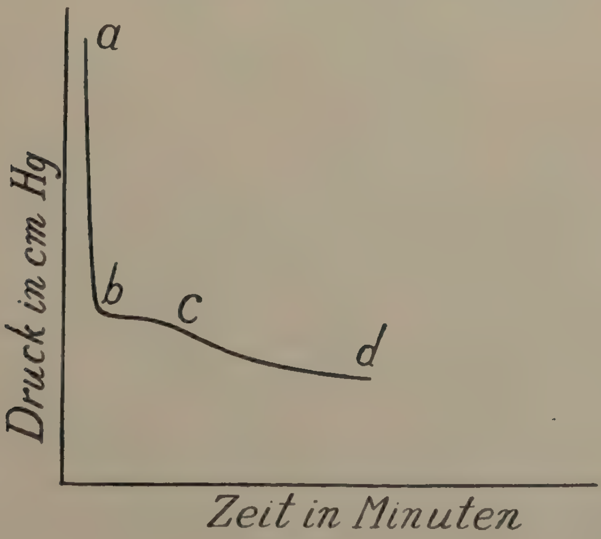

Fig. 3.

um *A* hatte eine schnelle Kondensation in *A* und *B* statt und der Dampfdruck sank mit grosser Geschwindigkeit.

Wenn nun der Stickstoff in *B* anfänglich etwas mehr von der meist flüchtigen Komponente, als in normalem Zustande, enthält und wenn diese Verschiedenheit durch rasche innere Umsetzungen bald wieder verschwindet, so wird der Dampfdruck erst rasch bis zu einem Wert, welcher etwas oberhalb des normalen Dampfdruckes liegt und danach, mit immer abnehmender Geschwindigkeit, bis zu dem normalen Wert sinken, wie es in Fig. 3 angegeben ist.

Das Resultat eines der gut gelungenen Versuche ist in folgender Tabelle wiedergegeben.

Temp. 77.9° abs.

Zeitdauer nach Ende der Destillation	Dampfdruck Destillat in cm Hg
5″	92.70
10″	81.00
30″	80.55
47″	80.52
1′ 5″	80.53
1′20″	80.50
1′35″	80.49
1′48″	80.45
2′05″	80.45
2′20″	80.41
2′35″	80.38
2′50″	80.40
3′ 5″	80.40

Tragen wir dieses Resultat in eine graphische Darstellung ein, so bekommen wir die folgende Kurve, Fig. 4. Diese Kurve stimmt in der Tat in groben Zügen mit der Kurve in Fig. 3 überein. Sie enthält einen 0.12 cm. Hg. oberhalb des Endwertes gelegenen Teil, wo der Druck praktisch 20 Sekunden konstant bleibt. Es kam auch vor, dass der Dampfdruck in obengenanntem Teil selbst ein Paar Zehntel mm. Hg. anzusteigen schien und dann erst wieder abnahm, doch in den meist gelungenen Experimenten war das nicht der Fall.

Nun könnte man meinen, dass es auch nicht gut einzusehen ist dass die Strecke bc *horizontal* sein kann, denn eine innere Umsetzung in der Richtung des inneren Gleichgewichts wird hier doch mit einer Abnahme des Dampfdruckes verbunden sein.

Nun ist hierbei folgendes zu bemerken. Wenn $N_{2\alpha}$ die meist flüchtige Pseudo-komponente und $N_{2\beta}$ die weniger flüchtige Pseudo-komponente des Stickstoffs ist, so wird bei der inneren Gleichgewichtseinstellung die Umsetzung

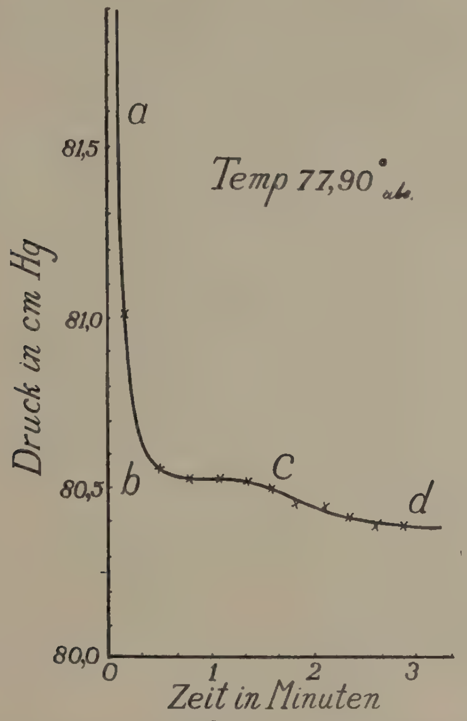

Fig. 4.

$$N_{2\alpha} \rightarrow N_{2\beta} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

im Destillat und in dem koexistierenden Dampf stattfinden und weil dabei der Dampfdruck abnimmt, wird eine sehr kleine Kondensation des Dampfes stattfinden müssen. Für den Fall, dass bei der Umsetzung (1) Wärme frei wird, so würde das Horizontal-sein von bc und selbst das Auftreten eines sehr schwachen Minimums und Maximums in dem Teil bc erklärlich sein. Der geringen Kondensationswärme brauchen wir hier höchstwahrscheinlich keine Rechnung zu tragen.

Während also eine Abdestillation der Hälfte ein Destillat lieferte, das bei der Temperatur des siedenden Stickstoffs die ersten Minuten einen Dampfdruck ± 0.10 cm. Hg höher, als derjenige des Restes zeigte, gab die sehr rasche Abdestillation einer sehr kleinen Quantität ein Destillat mit vorübergehend einen ± 0.12 cm. Hg. zu hohen Dampfdruck.

Diese erhaltenen Resultate stimmen nicht schlecht und würden darauf hinweisen, dass die Pseudo-komponenten des Stickstoffs, welche sehr wenig in Flüchtigkeit voneinander verschieden sein müssen, sich rasch in inneres

Gleichgewicht setzen, aber doch nicht so schnell, dass die Komplexität des Stickstoffs durch fraktionnierte Destillation unnachweisbar ist.

Die gefundenen Druckdifferenzen, worauf dieser Schluss sich stützt, sind aber sehr klein. Sie kommen mit einer Temperaturdifferenz von ± 0.025° überein und obwohl in unseren Stickstoffgefässe, während sie im Stickstoffbad getaucht waren, nach unseren Messungen mit dem Widerstandsthermometer innerhalb einiger Minuten nur Temperaturdifferenzen kleiner als 0.01° konstatiert worden sind, wollen wir doch hier mit Nachdruck betonen, dass wir die erhaltenen Resultate noch nicht als ein Beweis, aber nur als eine Anweisung hinsichtlich der Komplexität des Stickstoffs betrachten.

Die Experimenten werden fortgesetzt und dabei wird untersucht werden, welchen Einfluss intensive Trocknung hier ausübt.

Es sei hier kurz noch bemerkt, dass die Pseudo-figur des Stickstoffs, in Abweichung von der des Wasserstoffs, ein Entmischungsgebiet in dem festen Zustande enthalten wird, weil der Stickstoff einen Umwandlungspunkt zeigt 1). Drei mögliche Typen sind hier in die (T, X) Figuren 5, 6 und 7 gezeichnet.

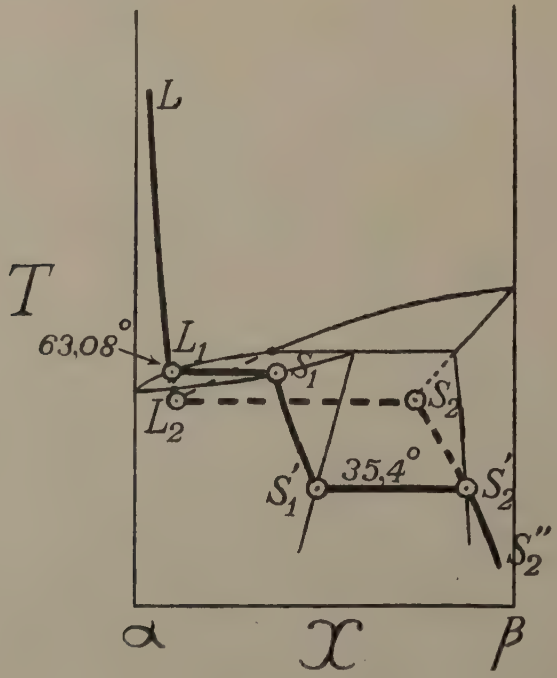

Fig. 5.

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1) Eucken, Verh. physik. Ges. 18, 4 (1915).
Keesom und Kamerlingh Onnes, Comm. Leiden 149*a*.
Clusius, Z.f. physik. Chem. B. 3, 41 (1929).

Die schwer gezogenen Linien geben wieder die Lage des unären Systems in dem Pseudo-System an. Von diesen Typen ist Fig. 5 wohl der meist wahrscheinliche Typus.

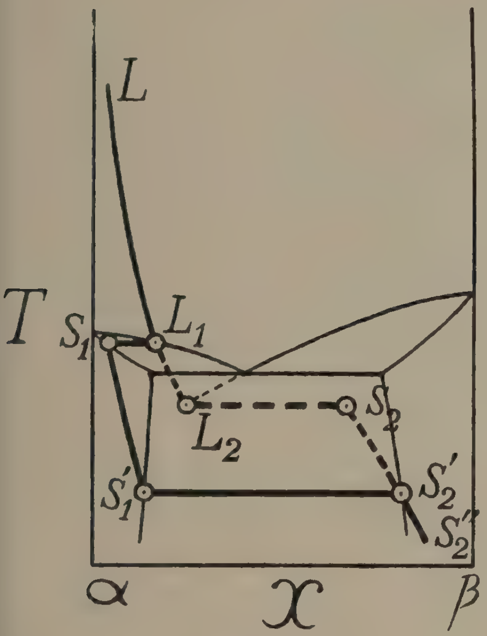

Fig. 6.

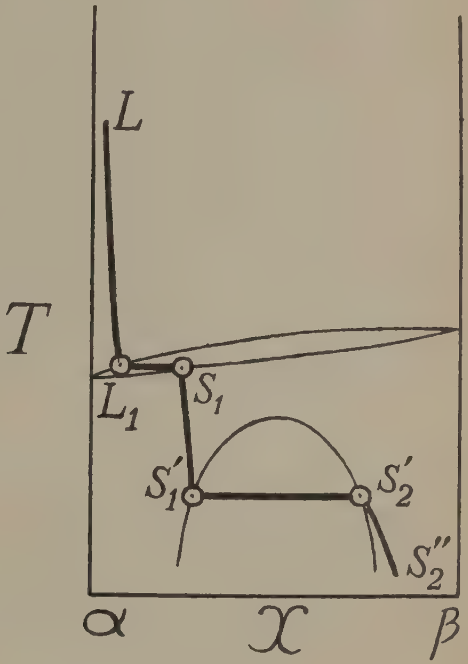

Fig. 7.

Schliesslich sei hier noch darauf hingewiesen, dass es stark verwirrend wirkt, von den zwei „Modifikationen" des Wasserstoffs u.s.w. zu sprechen, wenn man die zwei „Molekülarten" meint. In der physikalischen Chemie bezieht sich das Wort „Modifikation" *immer* auf die verschiedenen gleichartigen *Aggregatszustände* desselben Stoffes. Gleichartige Aggregatszustände hatte man bis vor kurzem nur bei dem besten Zustand gefunden. Helium gab uns das erste Beispiel eines Stoffes mit zwei flüssigen Aggregatszuständen oder zwei flüssigen „Modifikationen".

Eine *„Modifikation"* ist also immer eine *„Phase"* und nicht eine *Molekülart* oder *„Pseudo-komponente"*.

Im Stickstoff haben wir ein System mit vermutlich zwei „Molekülarten" oder „Pseudo-komponenten" und dabei hat der Stickstoff zwei feste „Modifikationen".

Laboratorium für allgemeine
und anorganische Chemie der Universität.

Amsterdam, Jan. 1930.

Mathematics. — *Sur la représentation conforme*. Par Prof. J. WOLFF. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of January 25, 1930).

Soit $w(z)$ une fonction donnant une représentation conforme de l'intérieur du cercle unité C du plan des z sur un domaine borné D du plan des w.

L'intégrale de $\left|\frac{dw}{dz}\right|^2$, étendue au domaine z est finie, d'où il resulte que, si α est un point arbitraire de C $(|\alpha| = 1)$, il existe une suite de nombres ϱ_n, décroissant vers zéro, tels que, γ_n étant l'arc de $|z-\alpha| = \varrho_n$, qui est intérieur à C:

$$\varrho_n \int_{\gamma_n} \left|\frac{dw}{dz}\right|^2 ds \rightarrow 0, \quad \text{pour} \quad n \rightarrow \infty,$$

car dans le cas contraire il existerait un nombre $\varepsilon > 0$, tel que, pour ϱ assez petit, on aurait

$$\int_{\gamma} \left|\frac{dw}{dz}\right|^2 ds > \varepsilon \varrho^{-1},$$

γ étant l'arc de $|z-\alpha| = \varrho$, qui est intérieur à C; donc l'intégrale de $\left|\frac{dw}{dz}\right|^2$, étendue au domaine $|z| < 1$, serait infinie.

Cela posé, on a

$$\int_{\gamma_n} \left|\frac{dw}{ds}\right| ds \leqq \left(\int_{\gamma_n} \left|\frac{dw}{dz}\right|^2 ds\right)^{1/2} \left(\int_{\gamma_n} 1^2\, ds\right)^{1/2} < \pi^{1/2} \varrho_n^{1/2} \left(\int_{\gamma_n} \left|\frac{dw}{dz}\right|^2 ds\right)^{1/2} \rightarrow 0.$$

Nous avons ainsi démontré l'existence d'une suite d'arcs circulaires γ_n se contractant vers α et tels que la longueur de l'image δ_n de γ_n tend vers zéro.

La coupure δ_n limite, avec une partie f_n de la frontière F de D, un domaine D_n qui se contracte quand n augmente. Le diamètre de D_n peut rester supérieur à un nombre fixe et on ne peut pas conclure que δ_n ait un point limite unique pour n infini.

Mais si F est une courbe simple de JORDAN, le diamètre de l'arc f_n tend vers zéro pour n infini, parceque la distance des extrémités de δ_n tend vers zéro. Il en suit que δ_n tend vers un point unique β, situé sur F, et que, quand z tend vers α, w tend vers β, et inversement:

c'est le théorème de l'existence des limites bi-univoques des fonctions $w(z)$ et $z(w)$ sur les frontières C et F.

Dans le cas général, à tout point α de C il correspond une portion f de F, limite de f_n pour n infini. En raisonnant sur les intégrales $\int_\delta \left|\frac{dz}{dw}\right| ds$ le long des arcs de cercle δ situés dans D et ayant pour centre un point β de F, comme nous avons raisonné sur les intégrales $\int_\gamma \left|\frac{dw}{dz}\right| ds$ le long des arcs de cercle γ situés dans C, nous voyons qu'il existe une suite de nombres ϱ_n décroissant vers zéro, tels que les arcs du cercle $|w-\beta|=\varrho_n$, situés dans D, sont les images d'arcs de courbe dans C, dont la somme des longueurs tend vers zéro pour n infini. L'ensemble limite de $z(w)$ en un point arbitraire β de F est donc une partie de C de mesure nulle. L'ensemble des points α de C, dont les portions correspondentes f de F contiennent un même point β, est par conséquent de mesure nulle.

Mathematics. — *Ueber Differentialinvarianten einer verallgemeinerten* GALILEI-NEWTON-*Gruppe* II. Von C. G. G. VAN HERK. (Communicated by Prof. R. WEITZENBÖCK).

(Communicated at the meeting of January 25, 1930).

§ 9. *Hilfsfunktionen.*

Zunächst wenden wir uns dem allgemeinen Fall des § 8 zu. Es sei also $m \geqslant 7$ und $\| C_i(p) \|$ eine Matrix dritten Ranges.

Die folgenden Hilfsfunktionen werden eingeführt:

$$E_{456} = \begin{vmatrix} C_1(4) & C_1(5) & C_1(6) \\ C_2(4) & C_2(5) & C_2(6) \\ C_3(4) & C_3(5) & C_3(6) \end{vmatrix} \quad . \quad . \quad . \quad . \quad (43)$$

$$\Gamma_{456} = \begin{vmatrix} \Gamma_1(4) & \Gamma_1(5) & \Gamma_1(6) \\ \Gamma_2(4) & \Gamma_2(5) & \Gamma_2(6) \\ \Gamma_3(4) & \Gamma_3(5) & \Gamma_3(6) \end{vmatrix} \quad . \quad . \quad . \quad , \quad (44)$$

$$H_7 = \begin{vmatrix} \triangle_4 & \triangle_5 & \triangle_6 & \triangle_7 \\ C_1(4) & C_1(5) & C_1(6) & C_1(7) \\ C_2(4) & C_2(5) & C_2(6) & C_2(7) \\ C_3(4) & C_3(5) & C_3(6) & C_3(7) \end{vmatrix} \quad . \quad . \quad . \quad (45)$$

$$G_{1\ldots6} = \begin{vmatrix} \mu_1 D_{\lambda_1, \mu_1-1, \nu_1+1} - \nu_1 D_{\lambda_1, \mu_1+1, \nu_1-1} \ldots \mu_6 D_{\lambda_6, \mu_6-1, \nu_6+1} - \nu_6 D_{\lambda_6, \mu_6+1, \nu_6-1} \\ \nu_1 D_{\lambda_1+1, \mu_1, \nu_1-1} - \lambda_1 D_{\lambda_1-1, \mu_1, \nu_1+1} \ldots \nu_6 D_{\lambda_6+1, \mu_6, \nu_6-1} - \lambda_6 D_{\lambda_6-1, \mu_6, \nu_6+1} \\ \lambda_1 D_{\lambda_1-1, \mu_1+1, \nu_1} - \mu_1 D_{\lambda_1+1, \mu_1-1, \nu_1} \ldots \lambda_6 D_{\lambda_6-1, \mu_6+1, \nu_6} - \mu_6 D_{\lambda_6+1, \mu_6-1, \nu_6} \\ D_{\lambda_1+1, \mu_1, \nu_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad D_{\lambda_6+1, \mu_6, \nu_6} \\ D_{\lambda_1, \mu_1+1, \nu_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad D_{\lambda_6, \mu_6+1, \nu_6} \\ D_{\lambda_1, \mu_1, \nu_1+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad D_{\lambda_6, \mu_6, \nu_6+1} \end{vmatrix} \quad (46)$$

$$R_{1\ldots7} = \begin{vmatrix} \mu_1 D_{\lambda_1, \mu_1-1, \nu_1+1} - \nu_1 D_{\lambda_1, \mu_1+1, \nu_1-1} \ldots \mu_7 D_{\lambda_7, \mu_7-1, \nu_7+1} - \nu_7 D_{\lambda_7, \mu_7+1, \nu_7-1} \\ \nu_1 D_{\lambda_1+1, \mu_1, \nu_1-1} - \lambda_1 D_{\lambda_1-1, \mu_1, \nu_1+1} \ldots \nu_7 D_{\lambda_7+1, \mu_7, \nu_7-1} - \lambda_7 D_{\lambda_7-1, \mu_7, \nu_7+1} \\ \lambda_1 D_{\lambda_1-1, \mu_1+1, \nu_1} - \mu_1 D_{\lambda_1+1, \mu_1-1, \nu_1} \ldots \lambda_7 D_{\lambda_7-1, \mu_7+1, \nu_7} - \mu_7 D_{\lambda_7+1, \mu_7-1, \nu_7} \\ D_{\lambda_1+1, \mu_1, \nu_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad D_{\lambda_7+1, \mu_7, \nu_7} \\ D_{\lambda_1, \mu_1+1, \nu_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad D_{\lambda_7, \mu_7+1, \nu_7} \\ D_{\lambda_1, \mu_1, \nu_1+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad D_{\lambda_7, \mu_7, \nu_7+1} \\ \dot{D}_{\lambda_1, \mu_1, \nu_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \dot{D}_{\lambda_7, \mu_7, \nu_7} \end{vmatrix} \quad (47)$$

Hier sollen die Indizes 1—7 in den Funktionen E, Γ, H, G und R Parametertripel $(\lambda_1 \mu_1 \nu_1) \ldots (\lambda_7 \mu_7 \nu_7)$ andeuten. Die Parameter λ, μ, ν sind wie zuvor ganze, nicht-negative Zahlen. Der einzige Index der H-Funktion soll andeuten, dass in diese Funktion 6 *unveränderliche* Tripel $(\lambda_1 \mu_1 \nu_1) \ldots (\lambda_6 \mu_6 \nu_6)$ eingehen, während z.B. in der Definition der R-Funktion jeder Tripelindex $i \, (i = 1 \ldots 7)$ durch jede beliebige andere Zahl zu ersetzen wäre.

Die Funktionen G und R, mit denen in der Folge hauptsächlich gearbeitet wird, sind keine algebraisch-unabhängigen Gröszen. Es ist:

$$G_{12\ldots6} = -G_{213\ldots6} \quad ; \quad R_{12\ldots7} = -R_{213\ldots7} \quad \text{u.s.f.}$$

Also wird insbesondere G oder R identisch Null, sobald zwei ihrer Parametertripel einander gleich sind. Im allgemeinen sind daher alle betrachteten Tripel als durchweg verschieden vorauszusetzen.

Ausserdem bestehen zwischen den verschiedenen Funktionen G bzw. R die sogenannten quadratischen p-Relationen [1].

Hilfssatz 2. Es gilt die Identität:

$$E_{ikl} = \nabla^2_{123} \, G_{123\,ikl} \quad \ldots\ldots\ldots \quad (48)$$

Beweis. Wir dürfen die Indizes (ikl) einfachheitshalber durch (456) ersetzen. Wegen (41) ist sodann:

$$E_{456} = \begin{vmatrix} \nabla_{234}\Gamma_1(1) - \nabla_{134}\Gamma_1(2) + \nabla_{124}\Gamma_1(3) - \nabla_{123}\Gamma_1(4) \quad \ldots \\ \ldots \quad \nabla_{236}\Gamma_1(1) - \nabla_{136}\Gamma_1(2) + \nabla_{126}\Gamma_1(3) - \nabla_{123}\Gamma_1(6) \\ \nabla_{234}\Gamma_2(1) - \nabla_{134}\Gamma_2(2) + \nabla_{124}\Gamma_2(3) - \nabla_{123}\Gamma_2(4) \quad \ldots \\ \ldots \quad \nabla_{236}\Gamma_2(1) - \nabla_{136}\Gamma_2(2) + \nabla_{126}\Gamma_2(3) - \nabla_{123}\Gamma_2(6) \\ \nabla_{234}\Gamma_3(1) - \nabla_{134}\Gamma_3(2) + \nabla_{124}\Gamma_3(3) - \nabla_{123}\Gamma_3(4) \quad \ldots \\ \ldots \quad \nabla_{236}\Gamma_3(1) - \nabla_{136}\Gamma_3(2) + \nabla_{126}\Gamma_3(3) - \nabla_{123}\Gamma_3(6) \end{vmatrix}$$

Zerfällt man die Elemente dieser Determinante in ihre Summanden $\nabla_{\alpha\beta\gamma}\,\Gamma_j\,(\delta)$, so erscheint E_{ikl} als Form $3 + 1$-ten Grades der Determinantenreihen $\nabla_{\alpha\beta\gamma}$ bzw. $\Gamma_{\alpha\beta\gamma}$, und einiges Umrechnen der Determinanten $\nabla_{\alpha\beta\gamma}$ mittels quadratischer p-Relationen gibt:

$$E_{456} = \nabla^2_{123} \cdot \left(\begin{array}{l} \nabla_{456}\Gamma_{123} - \nabla_{156}\Gamma_{234} + \nabla_{256}\Gamma_{134} - \nabla_{356}\Gamma_{124} + \nabla_{146}\Gamma_{235} - \\ - \nabla_{246}\Gamma_{135} + \nabla_{346}\Gamma_{125} - \nabla_{145}\Gamma_{236} + \nabla_{245}\Gamma_{136} - \nabla_{345}\Gamma_{126} + \\ + \nabla_{234}\Gamma_{156} - \nabla_{134}\Gamma_{256} + \nabla_{124}\Gamma_{356} - \nabla_{235}\Gamma_{146} + \nabla_{135}\Gamma_{246} - \\ - \nabla_{125}\Gamma_{346} + \nabla_{236}\Gamma_{145} - \nabla_{136}\Gamma_{245} + \nabla_{126}\Gamma_{345} - \nabla_{123}\Gamma_{456} \end{array} \right)$$

Alsdann gibt der Satz von LAPLACE die erwünschte Beziehung (48).

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[1] Vgl. R. WEITZENBÖCK, Invariantentheorie, Groningen (1923), S. 114 ff.

Hilfssatz 3. Es gilt die Identität:

$$H_q = \nabla^3_{123}\, R_{1\ldots 6q} \quad \ldots\ldots\ldots \quad (49)$$

Beweis. Beide Glieder der Gleichung (49) sind Linearformen der Ableitungen $\dot{D}_{\lambda\mu\nu}$ mit Koeffizienten, gebildet aus den verschiedenen Gröszen $D_{\lambda\mu\nu}$. Es genügt also die Gleichheit dieser Koeffizienten zu beweisen.

Ersetzt man wieder der Einfachheit halber q durch 7 so gilt:

$$(45) \quad \ldots \quad H_7 = \Delta_4 E_{567} - \Delta_5 E_{467} + \Delta_6 E_{457} - \Delta_7 E_{456}$$

$$(25)\ (26) \quad . \quad \Delta_p = \nabla_{23p} \dot{D}_1 - \nabla_{13p} \dot{D}_2 + \nabla_{12p} \dot{D}_3 - \nabla_{123} \dot{D}_p$$

Somit ist wegen (48):

$$H_7 = \nabla^2_{123} \cdot \left\{ \begin{array}{l} (\dot{D}_1 \nabla_{234} - \dot{D}_2 \nabla_{134} + \dot{D}_3 \nabla_{124} - \dot{D}_4 \nabla_{123})\, G_{123567} - \\ - (\dot{D}_1 \nabla_{235} - \dot{D}_2 \nabla_{135} + \dot{D}_3 \nabla_{125} - \dot{D}_5 \nabla_{123})\, G_{123467} + \\ + (\dot{D}_1 \nabla_{236} - \dot{D}_2 \nabla_{136} + \dot{D}_3 \nabla_{126} - \dot{D}_6 \nabla_{123})\, G_{123457} - \\ - (\dot{D}_1 \nabla_{237} - \dot{D}_2 \nabla_{137} + \dot{D}_3 \nabla_{127} - \dot{D}_7 \nabla_{123})\, G_{123456} \end{array} \right\}$$

Also ergibt sich (49) sofort als richtig was die Koeffizienten von $\dot{D}_4 \ldots \dot{D}_q$ betrifft; es genügt wegen der symmetrischen Anordnung der Indizes (123) dies auch noch für die Koeffizienten von $\dot{D}_3$ nachzuweisen, d.h. es soll die Beziehung:

$$\left. \begin{array}{r} \nabla_{123} G_{124567} - \nabla_{124} G_{123567} + \nabla_{125} G_{123467} - \nabla_{126} G_{123457} + \\ + \nabla_{127} G_{123456} = 0 \end{array} \right\} \quad (50)$$

identisch befriedigt werden.

Entwicklung nach LAPLACE gibt die Funktionen G als Linearformen der Gröszen $\Gamma_{\alpha\beta\gamma}$; die Koeffizienten dieser Gröszen in (50) sind quadratische Formen der Determinanten ∇, und müssen verschwinden. Die Symmetrieverhältnisse erlauben, die Betrachtung auf die Koeffizienten von Γ_{123}, Γ_{134} und Γ_{345} zu beschränken. Es soll also gelten:

$$-\nabla_{124} \nabla_{567} + \nabla_{125} \nabla_{467} - \nabla_{126} \nabla_{457} + \nabla_{127} \nabla_{456} = 0$$

bzw.:

$$\nabla_{125} \nabla_{267} - \nabla_{126} \nabla_{257} + \nabla_{127} \nabla_{256} = 0$$

und:

$$-\nabla_{126} \nabla_{127} + \nabla_{127} \nabla_{126} = 0.$$

Die letzte Gleichung ist trivial, die beiden ersten sind quadratische p-Relationen. Somit ist (49) bewiesen.

Es kann jetzt das allgemeine Integral K der Gleichungen (40) in einfacherer Gestalt dargestellt werden. Wegen der Voraussetzung über die Matrix $\| C_i\,(p) \|$ dürfen wir

$$E_{456} \not\equiv 0 \quad \ldots\ldots\ldots \quad (51)$$

annehmen.

Der Hilfssatz 1 ergibt sodann:

$$K = \Phi\{(\triangle_p)\ ;\ (D_{\alpha\beta\gamma})\} = \Psi\{(H_q)\ ;\ (D_{\alpha\beta\gamma})\}\ (7 \leqq q \leqq m)\ .\quad .\qquad (52)$$

wo $(\triangle_p)$, (H_q), $(D_{\alpha\beta\gamma})$ die Mengen der verschiedenen in Φ bzw. Ψ auftretenden Gröszen $\triangle$, H, D bezeichnen mögen.

Die Formel (52) lässt sich mittels (49) umformen. Es enthält ∇_{123} nur Gröszen $D_{\alpha\beta\gamma}$, d.h. es ist:

$$K = K\{(R_{1\ldots 6,\, q})\ ;\ (D_{\alpha\beta\gamma})\}\ .\ .\ .\ .\ .\ .\qquad (53)$$

die *notwendige Gestalt* einer Differentialinvariante K.

Es ist darauf hinzuweisen dass man in (53) die ersten 6 Parametertripel $(\lambda_i\, \mu_i\, \nu_i)$ $(i = 1\ldots 6)$ der verschiedenen in K auftretenden Gröszen R einen festen (willkürlichen) Wert geben kann. Diese 6 Tripel brauchen *nicht* explizite in der Darstellung (18) von K aufzutreten.

Man folgert dies sofort aus der, den quadratischen p-Relationen ähnlichen, Identität:

$$\left.\begin{aligned} &G_{1..6}\, R_{7890\alpha\beta\gamma} - G_{1..57}\, R_{6890\alpha\beta\gamma} + G_{1..58}\, R_{6790\alpha\beta\gamma} - \\ &- G_{1..59}\, R_{6780\alpha\beta\gamma} + G_{1..50}\, R_{6789\alpha\beta\gamma} - G_{1..5\alpha}\, R_{67890\beta\gamma} + \\ &+ G_{1..5\beta}\, R_{67890\alpha\gamma} - G_{1..5\gamma}\, R_{67890\alpha\beta} = 0 \end{aligned}\right\}\ .\qquad (54)$$

wo einige der 13 Tripel $(\lambda_i\, \mu_i\, \nu_i)$ $(i = 1\ldots 90\,\alpha\,\beta\,\gamma)$ einander gleich sein können. Notwendig ist nur, wie aus (54) folgt, *dass die aus den Tripeln 1 . . . 6 gebildete Funktion* $G_{1\ldots 6}$ *nicht identisch verschwindet.*

Diese Eigenschaft der ersten 6 Parametertripel der Funktionen R wird später eine wesentliche Vereinfachung des Problems herbeiführen.

§ 10. *Transformationsgleichungen.*

Die Gröszen G und R sind ziemlich verwickelte Funktionen der Ableitungen $D_{\lambda\mu\nu}$ und $\dot{D}_{\lambda\mu\nu}$, und es fragt sich jetzt:

„Bestehen für die Gröszen G und R Gleichungen der Gestalt:

$$G = G\{(\varepsilon_i),\ (\overline{G})\}\ ;\ R = R\{(\varepsilon_i),\ (\overline{R})\}\ .\ .\ .\ .\qquad (55)$$

wenn die unabhängig Veränderlichen (x_i, t) einer Transformation der Gruppe $\mathfrak{G}_2$ unterworfen werden?" [Die Mengen (ε_i), $(\overline{G})$, $(\overline{R})$ sollen wieder die verschiedenen in G bezw. R auftretenden Gröszen ε_i, $\overline{G}$ und $\overline{R}$ andeuten].

Ein solches Verhalten ist nicht ohne weiteres ersichtlich. Zwar wissen wir aus dem Vorhergehenden:

$$G = G\{(\varepsilon_i),\ (\overline{D}_{\lambda\mu\nu})\}\ ;\ R = R\{(\varepsilon_i),\ (D_{\lambda\mu\nu}),\ (\overline{\dot{D}}_{\lambda\mu\nu})\}\quad .\ .\qquad (56)$$

was für die Funktion G trivial ist, für die Funktion R aus dem Wegfallen der Transformationsparameter η_i und ε_i folgt; aber die Gleichung (55) besagt weit mehr als (56).

Die gestellte Frage ist zu bejahen. Zwecks ihrer Beantwortung seien erst einige Hilfssätze über eine Klasse von Funktionen bewiesen, Funktionen, die ich kurzweg als P-Funktionen andeuten will.

Definition. Es seien n Tripel $(u_i v_i w_i)$ $(i = 1 \ldots n;$ n willkürlich) von algebraisch-unabhängigen Variabeln $(u\, v\, w)$ gegeben. Eine Transformation T_2 der verallgemeinerten GALILEI-NEWTON-Gruppe $\mathfrak{G}_2$ (vgl. § 1) induziere eine orthogonale Transformation $(u_i v_i w_i) \rightarrow (\bar{u}_i \bar{v}_i \bar{w}_i)$ mit Koeffizienten e_{ik}:

$$\left.\begin{aligned} u_i &= e_{11}\,\bar{u}_i + e_{12}\,\bar{v}_i + e_{13}\,\bar{w}_i \\ v_i &= e_{21}\,\bar{u}_i + e_{22}\,\bar{v}_i + e_{23}\,\bar{w}_i \\ w_i &= e_{31}\,\bar{u}_i + e_{32}\,\bar{v}_i + e_{33}\,\bar{w}_i \end{aligned}\right\} \quad \ldots\ldots \quad (2')$$

Ferner seien die $3n$ Parameter $\lambda_i \mu_i \nu_i$ $(i = 1 \ldots n)$ ganze, nicht-negative Zahlen. Es soll sodann eine beliebige ganze und rationale Funktion F irgendwelcher Veränderlichen zur Klasse der P-Funktionen gehören, falls F durch eine Transformation T_2 der Veränderlichen $(x_i\, t)$ kogredient zum Produkt:

$$u_1^{\lambda_1}\, v_1^{\mu_1}\, w_1^{\nu_1}\, u_2^{\lambda_2} \ldots u_n^{\lambda_n}\, v_n^{\mu_n}\, w_n^{\nu_n}$$

transformiert wird.

Es wird also die Transformationsgleichung einer P-Funktion durch die n Parametertripel $(\lambda_i \mu_i \nu_i)$ genau bestimmt. Diese Tripel sind willkürlich, können also insbesondere einander gleich sein. Wird die Kogredienz bzgl. der Gruppe $\mathfrak{G}_0$ (vgl. § 1) durch das Symbol $\sim$ angedeutet, so kann man schreiben:

$$P\begin{bmatrix} \lambda_1 & \ldots & \lambda_n \\ \mu_1 & \ldots & \mu_n \\ \nu_1 & \ldots & \nu_n \end{bmatrix} \sim u_1^{\lambda_1}\, v_1^{\mu_1}\, w_1^{\nu_1}\, u_2^{\lambda_2} \ldots u_n^{\lambda_n}\, v_n^{\mu_n}\, w_n^{\nu_n} \quad \ldots \quad (57)$$

und die Transformationsgleichung lautet:

$$P\begin{bmatrix} \lambda_1 & \ldots & \lambda_n \\ \mu_1 & \ldots & \mu_n \\ \nu_1 & \ldots & \nu_n \end{bmatrix} = \sum_{(\alpha_1\beta_1\gamma_1)} \ldots \sum_{(\alpha_n\beta_n\gamma_n)} \pi\begin{pmatrix} \lambda_1\, \mu_1\, \nu_1 \\ \alpha_1\, \beta_1\, \gamma_1 \end{pmatrix} \ldots \pi\begin{pmatrix} \lambda_n\, \mu_n\, \nu_n \\ \alpha_n\, \beta_n\, \gamma_n \end{pmatrix} \overline{P}\begin{bmatrix} \alpha_1 & \ldots & \alpha_n \\ \beta_1 & \ldots & \beta_n \\ \gamma_1 & \ldots & \gamma_n \end{bmatrix} \quad (58)$$

wo die Summation zu erstrecken ist über alle Zahlentripel $(\alpha_i \beta_i \gamma_i)$ welche den Gleichungen:

$$\alpha_i \geqq 0; \quad \beta_i \geqq 0; \quad \gamma_i \geqq 0; \quad \alpha_i + \beta_i + \gamma_i = \lambda_i + \mu_i + \nu_i = \sigma_i \geqq 0 \quad (58')$$

genügen.

Die Funktion π ist wegen (2') (57) bestimmt durch die Gleichungen:

$$\pi\begin{pmatrix} \lambda\, \mu\, \nu \\ \alpha\, \beta\, \gamma \end{pmatrix} = \sum_{(\eta_{11} \ldots \eta_{33})} \frac{\lambda!\, \mu!\, \nu!}{\eta_{11}!\, \eta_{12}! \ldots \eta_{33}!}\, e_{11}^{\eta_{11}}\, e_{12}^{\eta_{12}} \ldots e_{33}^{\eta_{33}} \quad \ldots \quad (59)$$

$$\left.\begin{aligned} &\qquad\qquad\qquad\qquad \eta_{ik} \geqq 0 \\ &\eta_{11} + \eta_{12} + \eta_{13} = \lambda \qquad \eta_{21} + \eta_{22} + \eta_{23} = \mu \qquad \eta_{31} + \eta_{32} + \eta_{33} = \nu \\ &\eta_{11} + \eta_{21} + \eta_{31} = \alpha \qquad \eta_{12} + \eta_{22} + \eta_{32} = \beta \qquad \eta_{13} + \eta_{23} + \eta_{33} = \gamma \end{aligned}\right\} \quad (59')$$

Ein einfachstes Beispiel einer *P*-Funktion bietet die Grösze:

$$D_{\lambda\mu\nu} = \frac{\partial^{\lambda+\mu+\nu}\varphi}{\partial x_1^{\lambda}\,\partial x_2^{\mu}\,\partial x_3^{\nu}}.$$

Sie besitzt wegen (13) die Transformationsgleichung:

$$D_{\lambda\mu\nu} = \sum_{(\alpha\beta\gamma)} \pi\begin{pmatrix}\lambda\,\mu\,\nu\\ \alpha\,\beta\,\gamma\end{pmatrix}\overline{D}_{\alpha\beta\gamma}\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (60)$$

und ist zu $u^{\lambda}\,v^{\mu}\,w^{\nu}$ kogredient.

Hilfssatz 4. Die Summe zweier, von denselben Parametertripeln abhängigen *P*-Funktionen ist wieder eine *P*-Funktion:

$$P_1\left[\begin{matrix}\lambda_1 & \dots & \lambda_n\\ \mu_1 & \dots & \mu_n\\ \nu_1 & \dots & \nu_n\end{matrix}\right] + P_2\left[\begin{matrix}\lambda_1 & \dots & \lambda_n\\ \mu_1 & \dots & \mu_n\\ \nu_1 & \dots & \nu_n\end{matrix}\right] = P_3\left[\begin{matrix}\lambda_1 & \dots & \lambda_n\\ \mu_1 & \dots & \mu_n\\ \nu_1 & \dots & \nu_n\end{matrix}\right].$$

Beweis. Ist wegen (58) trivial.

Hilfssatz 5. Das Produkt zweier *P*-Funktionen ist eine *P*-Funktion:

$$P_1\left[\begin{matrix}\lambda_1 & \dots & \lambda_n\\ \mu_1 & \dots & \mu_n\\ \nu_1 & \dots & \nu_n\end{matrix}\right] \cdot P_2\left[\begin{matrix}\lambda_{n+1} & \dots & \lambda_m\\ \mu_{n+1} & \dots & \mu_m\\ \nu_{n+1} & \dots & \nu_m\end{matrix}\right] = P_3\left[\begin{matrix}\lambda_1 & \dots & \lambda_m\\ \mu_1 & \dots & \mu_m\\ \nu_1 & \dots & \nu_m\end{matrix}\right].$$

Beweis. Ist wegen (58) trivial.

Das nächste Ziel ist jetzt, zu beweisen, dass die Funktionen G und R *P*-Funktionen sind; alsdann wird auch die Gleichung (55) erfüllt, wie aus dem Obigem ersichtlich.

§ 11. *Spezielle P-Funktionen.*

Hilfssatz 6. Die Funktion ∇ ist eine *P*-Funktion:[1]

$$\nabla_{123} = \nabla\left[\begin{matrix}\lambda_1 & \lambda_2 & \lambda_3\\ \mu_1 & \mu_2 & \mu_3\\ \nu_1 & \nu_2 & \nu_3\end{matrix}\right] \sim u_1^{\lambda_1}\,v_1^{\mu_1}\dots w_3^{\nu_3}.$$

---

[1] Anmerkung: für uneigentlich orthogonale Transformationen (2′) kommt noch ein Zeichenwechsel in der Transformationsgleichung der Funktion ∇ hinzu; dasselbe gilt für die Transformationsgleichung der Funktion Γ_{ikl}; in der *G*-Funktion heben sich diese Zeichenwechsel gegenseitig auf. Es werden hier nur eigentlich orthogonale Transformationen (2′) betrachtet.

Beweis. Es ist wegen (11), (24):

$$\nabla_{123} = \frac{\partial (D_1\, D_2\, D_3)}{\partial (\overline{x}_1\, \overline{x}_2\, \overline{x}_3)} =$$

$$= \begin{vmatrix} e_{11} \frac{\partial D_1}{\partial \overline{x}_1} + e_{12} \frac{\partial D_1}{\partial \overline{x}_2} + e_{13} \frac{\partial D_1}{\partial \overline{x}_3} & \ldots & e_{11} \frac{\partial D_3}{\partial \overline{x}_1} + e_{12} \frac{\partial D_3}{\partial \overline{x}_2} + e_{13} \frac{\partial D_3}{\partial \overline{x}_3} \\ e_{21} \frac{\partial D_1}{\partial \overline{x}_1} + e_{22} \frac{\partial D_1}{\partial \overline{x}_2} + e_{23} \frac{\partial D_1}{\partial \overline{x}_3} & \ldots & e_{21} \frac{\partial D_3}{\partial \overline{x}_1} + e_{22} \frac{\partial D_3}{\partial \overline{x}_2} + e_{23} \frac{\partial D_3}{\partial \overline{x}_3} \\ e_{31} \frac{\partial D_1}{\partial \overline{x}_1} + e_{32} \frac{\partial D_1}{\partial \overline{x}_2} + e_{33} \frac{\partial D_1}{\partial \overline{x}_3} & \ldots & e_{31} \frac{\partial D_3}{\partial \overline{x}_1} + e_{32} \frac{\partial D_3}{\partial \overline{x}_2} + e_{33} \frac{\partial D_3}{\partial \overline{x}_3} \end{vmatrix} =$$

$$= \begin{vmatrix} e_{11} & e_{12} & e_{13} \\ e_{21} & e_{22} & e_{23} \\ e_{31} & e_{32} & e_{33} \end{vmatrix} \cdot \begin{vmatrix} \frac{\partial D_1}{\partial \overline{x}_1} & \frac{\partial D_2}{\partial \overline{x}_1} & \frac{\partial D_3}{\partial \overline{x}_1} \\ \frac{\partial D_1}{\partial \overline{x}_2} & \frac{\partial D_2}{\partial \overline{x}_2} & \frac{\partial D_3}{\partial \overline{x}_2} \\ \frac{\partial D_1}{\partial \overline{x}_3} & \frac{\partial D_2}{\partial \overline{x}_3} & \frac{\partial D_3}{\partial \overline{x}_3} \end{vmatrix} = \begin{vmatrix} \frac{\partial D_1}{\partial \overline{x}_1} & \frac{\partial D_2}{\partial \overline{x}_1} & \frac{\partial D_3}{\partial \overline{x}_1} \\ \frac{\partial D_1}{\partial \overline{x}_2} & \frac{\partial D_2}{\partial \overline{x}_2} & \frac{\partial D_3}{\partial \overline{x}_3} \\ \frac{\partial D_1}{\partial \overline{x}_3} & \frac{\partial D_2}{\partial \overline{x}_3} & \frac{\partial D_3}{\partial \overline{x}_3} \end{vmatrix}$$

Wendet man hierauf die Formel (60) an, so bekommt man:

$$\nabla \begin{bmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ \mu_1 & \mu_2 & \mu_3 \\ \nu_1 & \nu_2 & \nu_3 \end{bmatrix} = \begin{vmatrix} \sum\limits_{(\alpha_1 \beta_1 \gamma_1)} \pi \begin{pmatrix} \lambda_1 & \mu_1 & \nu_1 \\ \alpha_1 & \beta_1 & \gamma_1 \end{pmatrix} \frac{\partial \overline{D}_{\alpha_1 \beta_1 \gamma_1}}{\partial \overline{x}_1} & \ldots & \sum\limits_{(\alpha_3 \beta_3 \gamma_3)} \pi \begin{pmatrix} \lambda_3 & \mu_3 & \nu_3 \\ \alpha_3 & \beta_3 & \gamma_3 \end{pmatrix} \frac{\partial \overline{D}_{\alpha_3 \beta_3 \gamma_3}}{\partial \overline{x}_1} \\ \sum\limits_{(\alpha_1 \beta_1 \gamma_1)} \pi \begin{pmatrix} \lambda_1 & \mu_1 & \nu_1 \\ \alpha_1 & \beta_1 & \gamma_1 \end{pmatrix} \frac{\partial \overline{D}_{\alpha_1 \beta_1 \gamma_1}}{\partial \overline{x}_2} & \ldots & \sum\limits_{(\alpha_3 \beta_3 \gamma_3)} \pi \begin{pmatrix} \lambda_3 & \mu_3 & \nu_3 \\ \alpha_3 & \beta_3 & \gamma_3 \end{pmatrix} \frac{\partial \overline{D}_{\alpha_3 \beta_3 \gamma_3}}{\partial \overline{x}_2} \\ \sum\limits_{(\alpha_1 \beta_1 \gamma_1)} \pi \begin{pmatrix} \lambda_1 & \mu_1 & \nu_1 \\ \alpha_1 & \beta_1 & \gamma_1 \end{pmatrix} \frac{\partial \overline{D}_{\alpha_1 \beta_1 \gamma_1}}{\partial \overline{x}_3} & \ldots & \sum\limits_{(\alpha_3 \beta_3 \gamma_3)} \pi \begin{pmatrix} \lambda_3 & \mu_3 & \nu_3 \\ \alpha_3 & \beta_3 & \gamma_3 \end{pmatrix} \frac{\partial \overline{D}_{\alpha_3 \beta_3 \gamma_3}}{\partial \overline{x}_3} \end{vmatrix} =$$

$$= \sum_{(\alpha_1 \beta_1 \gamma_1)} \ldots \sum_{(\alpha_3 \beta_3 \gamma_3)} \pi \begin{pmatrix} \lambda_1 & \mu_1 & \nu_1 \\ \alpha_1 & \beta_1 & \gamma_1 \end{pmatrix} \ldots \pi \begin{pmatrix} \lambda_3 & \mu_3 & \nu_3 \\ \alpha_3 & \beta_3 & \gamma_3 \end{pmatrix} \frac{\partial (\overline{D}_{\alpha_1 \beta_1 \gamma_1}\, \overline{D}_{\alpha_2 \beta_2 \gamma_2}\, \overline{D}_{\alpha_3 \beta_3 \gamma_3})}{\partial (\overline{x}_1\, \overline{x}_2\, \overline{x}_3)} =$$

$$= \sum_{(\alpha_1 \beta_1 \gamma_1)} \ldots \sum_{(\alpha_3 \beta_3 \gamma_3)} \pi \begin{pmatrix} \lambda_1 & \mu_1 & \nu_1 \\ \alpha_1 & \beta_1 & \gamma_1 \end{pmatrix} \ldots \pi \begin{pmatrix} \lambda_3 & \mu_3 & \nu_3 \\ \alpha_3 & \beta_3 & \gamma_3 \end{pmatrix} \overline{\nabla} \begin{bmatrix} \alpha_1 & \alpha_2 & \alpha_3 \\ \beta_1 & \beta_2 & \beta_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{bmatrix}$$

q.e.d.

Hilfssatz 7. Die Funktion Γ_{ikl} ist eine P-Funktion:

$$\Gamma_{123} = \Gamma \begin{bmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ \mu_1 & \mu_2 & \mu_3 \\ \nu_1 & \nu_2 & \nu_3 \end{bmatrix} \sim u_1^{\lambda_1}\, v_1^{\mu_1} \ldots w_3^{\nu_3}.$$

Beweis. Die zu beweisende Formel lautet:

$$\Gamma\begin{bmatrix}\lambda_1 & \lambda_2 & \lambda_3\\ \mu_1 & \mu_2 & \mu_3\\ \nu_1 & \nu_2 & \nu_3\end{bmatrix}=\sum_{(\alpha_1\beta_1\lambda_1)}\cdots\sum_{(\alpha_3\beta_3\gamma_3)}\pi\begin{pmatrix}\lambda_1 & \mu_1 & \nu_1\\ \alpha_1 & \beta_1 & \gamma_1\end{pmatrix}\cdots\pi\begin{pmatrix}\lambda_3 & \mu_3 & \nu_3\\ \alpha_3 & \beta_3 & \gamma_3\end{pmatrix}\overline{\Gamma}\begin{bmatrix}\alpha_1 & \alpha_2 & \alpha_3\\ \beta_1 & \beta_2 & \beta_3\\ \gamma_1 & \gamma_2 & \gamma_3\end{bmatrix}\qquad(61)$$

wo wegen (38), (42), (44):

$$\Gamma\begin{bmatrix}\lambda_1 & \lambda_2 & \lambda_3\\ \mu_1 & \mu_2 & \mu_3\\ \nu_1 & \nu_2 & \nu_3\end{bmatrix}=$$

$$\begin{vmatrix}\mu_1 D_{\lambda_1,\mu_1-1,\nu_1+1}-\nu_1 D_{\lambda_1,\mu_1+1,\nu_1-1} & \ldots & \mu_3 D_{\lambda_3,\mu_3-1,\nu_3+1}-\nu_3 D_{\lambda_3,\mu_3+1,\nu_3-1}\\ \nu_1 D_{\lambda_1+1,\mu_1,\nu_1-1}-\lambda_1 D_{\lambda_1-1,\mu_1,\nu_1+1} & \ldots & \nu_3 D_{\lambda_3+1,\mu_3,\nu_3-1}-\lambda_3 D_{\lambda_3-1,\mu_3,\nu_3+1}\\ \lambda_1 D_{\lambda_1-1,\mu_1+1,\nu_1}-\mu_1 D_{\lambda_1+1,\mu_1-1,\nu_1} & \ldots & \lambda_3 D_{\lambda_3-1,\mu_3+1,\nu_3}-\mu_3 D_{\lambda_3+1,\mu_3-1,\nu_3}\end{vmatrix}\ .\qquad(62)$$

und wegen (58′):

$$\alpha_i+\beta_i+\gamma_i=\lambda_i+\mu_i+\nu_i=\sigma_i\geqq 0\qquad(i=1,2,3)\quad.\quad(62')$$

ist. Es ist gleichgültig ob die Zahlen σ_i von einander verschieden sind oder nicht.

Wendet man die Transformation (60) an, so erscheinen beide Glieder in (61) als kubische Formen von Gröszen $\overline{D}_{\lambda\mu\nu}$. Es ist daher für das erste bzw. zweite Glied von (61) zu schreiben:

$$\left.\begin{aligned}&\sum_{(p_1q_1r_1)}\cdots\sum_{(p_3q_3r_3)}c\begin{bmatrix}p_1 & p_2 & p_3\\ q_1 & q_2 & q_3\\ r_1 & r_2 & r_3\end{bmatrix}\overline{D}_{p_1q_1r_1}\overline{D}_{p_2q_2r_2}\overline{D}_{p_3q_3r_3}\\ \text{und:}\\ &\sum_{(p_1q_1r_1)}\cdots\sum_{(p_3q_3r_3)}c'\begin{bmatrix}p_1 & p_2 & p_3\\ q_1 & q_2 & q_3\\ r_1 & r_2 & r_3\end{bmatrix}\overline{D}_{p_1q_1r_1}\overline{D}_{p_2q_2r_2}\overline{D}_{p_3q_3r_3}\end{aligned}\right\}\quad\ldots\quad(63)$$

wo die Summation über alle (pqr), für welche:

$$p_i\geqq 0;\quad q_i\geqq 0;\quad r_i\geqq 0;\quad p_i+q_i+r_i=\sigma_i\qquad(i=1,2,3)\quad(63')$$

zu erstrecken ist. Man hat dann nur zu beweisen:

$$c\begin{bmatrix}p_1 & p_2 & p_3\\ q_1 & q_2 & q_3\\ r_1 & r_2 & r_3\end{bmatrix}=c'\begin{bmatrix}p_1 & p_2 & p_3\\ q_1 & q_2 & q_3\\ r_1 & r_2 & r_3\end{bmatrix}\quad.\ .\ .\ .\ .\ .\ .\quad(64)$$

Aus (60), (62), (63) erhält man die Darstellung:

$$c\begin{vmatrix} p_1 & p_2 & p_3 \\ q_1 & q_2 & q_3 \\ r_1 & r_2 & r_3 \end{vmatrix} =$$

$$= \begin{vmatrix} \dfrac{\partial(\mu_1 D_{\lambda_1,\mu_1-1,\nu_1+1} - \nu_1 D_{\lambda_1,\mu_1+1,\nu_1-1})}{\partial \bar{\bar{D}}_{p_1q_1r_1}} & \cdot\cdot & \dfrac{\partial(\mu_3 D_{\lambda_3,\mu_3-1,\nu_3+1} - \nu_3 D_{\lambda_3,\mu_3+1,\nu_3-1})}{\partial \bar{\bar{D}}_{p_3q_3r_3}} \\ \dfrac{\partial(\nu_1 D_{\lambda_1+1,\mu_1,\nu_1-1} - \lambda_1 D_{\lambda_1-1,\mu_1,\nu_1+1})}{\partial \bar{\bar{D}}_{p_1q_1r_1}} & \cdot\cdot & \dfrac{\partial(\nu_3 D_{\lambda_3+1,\mu_3,\nu_3-1} - \lambda_3 D_{\lambda_3-1,\mu_3,\nu_3+1})}{\partial \bar{\bar{D}}_{p_3q_3r_3}} \\ \dfrac{\partial(\lambda_1 D_{\lambda_1-1,\mu_1+1,\nu_1} - \mu_1 D_{\lambda_1+1,\mu_1-1,\nu_1})}{\partial \bar{\bar{D}}_{p_1q_1r_1}} & \cdot\cdot & \dfrac{\partial(\lambda_3 D_{\lambda_3-1,\mu_3+1,\nu_3} - \mu_3 D_{\lambda_3+1,\mu_3-1,\nu_3})}{\partial \bar{\bar{D}}_{p_3q_3r_3}} \end{vmatrix} =$$

$$= \begin{vmatrix} \mu_1\,\pi\begin{pmatrix}\lambda_1 & \mu_1-1 & \nu_1+1 \\ p_1 & q_1 & r_1\end{pmatrix} - \nu_1\,\pi\begin{pmatrix}\lambda_1 & \mu_1+1 & \nu_1-1 \\ p_1 & q_1 & r_1\end{pmatrix} \cdots \\ \cdots\ \mu_3\,\pi\begin{pmatrix}\lambda_3 & \mu_3-1 & \nu_3+1 \\ p_3 & q_3 & r_3\end{pmatrix} - \nu_3\,\pi\begin{pmatrix}\lambda_3 & \mu_3+1 & \nu_3-1 \\ p_3 & q_3 & r_3\end{pmatrix} \\ \nu_1\,\pi\begin{pmatrix}\lambda_1+1 & \mu_1 & \nu_1-1 \\ p_1 & q_1 & r_1\end{pmatrix} - \lambda_1\,\pi\begin{pmatrix}\lambda_1-1 & \mu_1 & \nu_1+1 \\ p_1 & q_1 & r_1\end{pmatrix} \cdots \\ \cdots\ \nu_3\,\pi\begin{pmatrix}\lambda_3+1 & \mu_3 & \nu_3-1 \\ p_3 & q_3 & r_3\end{pmatrix} - \lambda_3\,\pi\begin{pmatrix}\lambda_3-1 & \mu_3 & \nu_3+1 \\ p_3 & q_3 & r_3\end{pmatrix} \\ \lambda_1\,\pi\begin{pmatrix}\lambda_1-1 & \mu_1+1 & \nu_1 \\ p_1 & q_1 & r_1\end{pmatrix} - \mu_1\,\pi\begin{pmatrix}\lambda_1+1 & \mu_1-1 & \nu_1 \\ p_1 & q_1 & r_1\end{pmatrix} \cdots \\ \cdots\ \lambda_3\,\pi\begin{pmatrix}\lambda_3-1 & \mu_3+1 & \nu_3 \\ p_3 & q_3 & r_3\end{pmatrix} - \mu_3\,\pi\begin{pmatrix}\lambda_3+1 & \mu_3-1 & \nu_3 \\ p_3 & q_3 & r_3\end{pmatrix} \end{vmatrix} \qquad (65)$$

Eine ähnliche Darstellung läszt sich für c' gewinnen. Man bekommt:

$$c'\begin{vmatrix} p_1 & p_2 & p_3 \\ q_1 & q_2 & q_3 \\ r_1 & r_2 & r_3 \end{vmatrix} = \sum_{(\alpha_1\beta_1\gamma_1)} \cdots \sum_{(\alpha_3\beta_3\gamma_3)} \pi\begin{pmatrix}\lambda_1 & \mu_1 & \nu_1 \\ \alpha_1 & \beta_1 & \gamma_1\end{pmatrix} \cdots \pi\begin{pmatrix}\lambda_3 & \mu_3 & \nu_3 \\ \alpha_3 & \beta_3 & \gamma_3\end{pmatrix} \times$$

$$\times \begin{vmatrix} \dfrac{\partial(\beta_1 \bar{D}_{\alpha_1,\beta_1-1,\gamma_1+1} - \gamma_1 \bar{D}_{\alpha_1,\beta_1+1,\gamma_1-1})}{\partial \bar{\bar{D}}_{p_1q_1r_1}} & \cdot\cdot & \dfrac{\partial(\beta_3 \bar{D}_{\alpha_3,\beta_3-1,\gamma_3+1} - \gamma_3 \bar{D}_{\alpha_3,\beta_3+1,\gamma_3-1})}{\partial \bar{\bar{D}}_{p_3q_3r_3}} \\ \dfrac{\partial(\gamma_1 D_{\alpha_1+1,\beta_1,\gamma_1-1} - \alpha_1 \bar{D}_{\alpha_1-1,\beta_1,\gamma_1+1})}{\partial \bar{\bar{D}}_{p_1q_1r_1}} & \cdot\cdot & \dfrac{\partial(\gamma_3 \bar{D}_{\alpha_3+1,\beta_3,\gamma_3-1} - \alpha_3 \bar{D}_{\alpha_3-1,\beta_3,\gamma_3+1})}{\partial \bar{\bar{D}}_{p_3q_3r_3}} \\ \dfrac{\partial(\alpha_1 \bar{D}_{\alpha_1-1,\beta_1+1,\gamma_1} - \beta_1 D_{\alpha_1+1,\beta_1-1,\gamma_1}}{\partial \bar{\bar{D}}_{p_1q_1r_1}} & \cdot\cdot & \dfrac{\partial(\alpha_3 \bar{D}_{\alpha_3-1,\beta_3+1,\gamma_3} - \beta_3 \bar{D}_{\alpha_3+1,\beta_3-1,\gamma_3})}{\partial \bar{\bar{D}}_{p_3q_3r_3}} \end{vmatrix} = \qquad (66)$$

$$= \sum_{(\alpha_1\beta_1\gamma_1)} \cdots \sum_{(\alpha_3\beta_3\gamma_3)} \pi\begin{pmatrix}\lambda_1 & \mu_1 & \nu_1 \\ \alpha_1 & \beta_1 & \gamma_1\end{pmatrix} \cdots \pi\begin{pmatrix}\lambda_3 & \mu_3 & \nu_3 \\ \alpha_3 & \beta_3 & \gamma_3\end{pmatrix} \times$$

$$\left.\begin{array}{l}
\times\left|\begin{array}{l}
\beta_1\,\delta_{p_1,\alpha_1}\;\delta_{q_1,\beta_1-1}\;\delta_{r_1,\gamma_1+1}-\gamma_1\,\delta_{p_1,\alpha_1}\;\delta_{q_1,\beta_1+1}\;\delta_{r_1,\gamma_1-1}\;\ldots\\
\qquad\qquad\ldots\beta_3\,\delta_{p_3,\alpha_3}\;\delta_{q_3,\beta_3-1}\;\delta_{r_3,\gamma_3+1}-\gamma_3\,\delta_{p_3,\alpha_3}\;\delta_{q_3,\beta_3+1}\;\delta_{r_3,\gamma_3-1}\\
\gamma_1\,\delta_{p_1,\alpha_1+1}\;\delta_{q_1,\beta_1}\;\delta_{r_1,\gamma_1-1}-\alpha_1\,\delta_{p_1,\alpha_1-1}\;\delta_{q_1,\beta_1}\;\delta_{r_1,\gamma_1+1}\;\ldots\\
\qquad\qquad\ldots\gamma_3\,\delta_{p_3,\alpha_3+1}\;\delta_{q_3,\beta_3}\;\delta_{r_3,\gamma_3-1}-\alpha_3\,\delta_{p_3,\alpha_3-1}\;\delta_{q_3,\beta_3}\;\delta_{r_3,\gamma_3+1}\\
\alpha_1\,\delta_{p_1,\alpha_1-1}\;\delta_{q_1,\beta_1+1}\;\delta_{r_1,\gamma_1}-\beta_1\,\delta_{p_1,\alpha_1+1}\;\delta_{q_1,\beta_1-1}\;\delta_{r_1,\gamma_1}\;\ldots\\
\qquad\qquad\ldots\alpha_3\,\delta_{p_3,\alpha_3-1}\;\delta_{q_3,\beta_3+1}\;\delta_{r_3,\nu_3}-\beta_3\,\delta_{p_3,\alpha_3+1}\;\delta_{q_3,\beta_3-1}\;\delta_{r_3,\gamma_3}
\end{array}\right|=\\[2ex]
=\left|\begin{array}{l}
(q_1+1)\,\pi\begin{pmatrix}\lambda_1 & \mu_1 & \nu_1\\ p_1 & q_1+1 & r_1-1\end{pmatrix}-(r_1+1)\,\pi\begin{pmatrix}\lambda_1 & \mu_1 & \nu_1\\ p_1 & q_1-1 & r_1+1\end{pmatrix}\ldots\\
\ldots(q_3+1)\,\pi\begin{pmatrix}\lambda_3 & \mu_3 & \nu_3\\ p_3 & q_3+1 & r_3-1\end{pmatrix}-(r_3+1)\,\pi\begin{pmatrix}\lambda_3 & \mu_3 & \nu_3\\ p_3 & q_3-1 & r_3+1\end{pmatrix}\\
(r_1+1)\,\pi\begin{pmatrix}\lambda_1 & \mu_1 & \nu_1\\ p_1-1 & q_1 & r_1+1\end{pmatrix}-(p_1+1)\,\pi\begin{pmatrix}\lambda_1 & \mu_1 & \nu_1\\ p_1+1 & q_1 & r_1-1\end{pmatrix}\ldots\\
\ldots(r_3+1)\,\pi\begin{pmatrix}\lambda_3 & \mu_3 & \nu_3\\ p_3-1 & q_3 & r_3+1\end{pmatrix}-(p_3+1)\,\pi\begin{pmatrix}\lambda_3 & \mu_3 & \nu_3\\ p_3+1 & q_3 & r_3-1\end{pmatrix}\\
(p_1+1)\,\pi\begin{pmatrix}\lambda_1 & \mu_1 & \nu_1\\ p_1+1 & q_1-1 & r_1\end{pmatrix}-(q_1+1)\,\pi\begin{pmatrix}\lambda_1 & \mu_1 & \nu_1\\ p_1-1 & q_1+1 & r_1\end{pmatrix}\ldots\\
\ldots(p_3+1)\,\pi\begin{pmatrix}\lambda_3 & \mu_3 & \nu_3\\ p_3+1 & q_3-1 & r_3\end{pmatrix}-(q_3+1)\,\pi\begin{pmatrix}\lambda_3 & \mu_3 & \nu_3\\ p_3-1 & q_3+1 & r_3\end{pmatrix}
\end{array}\right|
\end{array}\right\}\quad(66)$$

Hier ist wieder

$$\delta_{ik}=\begin{cases}0 \text{ für } i\neq k\\ 1 \quad ,, \quad i=k.\end{cases}$$

Für negative Argumentwerte ist die Funktion π in (66) gleich Null zu setzen.

Es genügt jetzt die Gleichheit der Determinanten (65), (66) zu beweisen. Gemäss (59), (59′) war die Funktion π für nicht-negative Argumentwerte bestimmt durch die Gleichung:

$$\pi\begin{pmatrix}\lambda\,\mu\,\nu\\ \alpha\,\beta\,\gamma\end{pmatrix}=\frac{\partial\,(u^\lambda\, v^\mu\, w^\nu)}{\partial\,(\bar{u}^\alpha\, \bar{v}^\beta\, \bar{w}^\gamma)};\ \alpha+\beta+\gamma=\lambda+\mu+\nu=\sigma\geqq 0\,. \quad . \quad (67)$$

wenn die Veränderlichen $(u\,v\,w)$ durch eine Gleichung (2′) mit den Veränderlichen $(\bar{u}\,\bar{v}\,\bar{w})$ zusammenhängen.

Es sei für *willkürliche* nicht-negative ganze Zahlen $(\alpha,\ \beta\ldots\nu)$:

$$\Pi^{\lambda\mu\nu}_{\alpha\beta\gamma}=\frac{\partial^{\alpha+\beta+\gamma}\,(u^\lambda\, v^\mu\, w^\nu\,)}{\partial\bar{u}^\alpha\,\partial\bar{v}^\beta\,\partial\bar{w}^\gamma}.\quad .\ .\ .\ .\ .\ .\ .\quad (68)$$

also für $\alpha+\beta+\gamma=\lambda+\mu+\nu$:

$$(67)\ .\ .\ .\ .\ .\ .\ .\ .\quad \pi\begin{pmatrix}\lambda\,\mu\,\nu\\ \alpha\,\beta\,\gamma\end{pmatrix}=\frac{1}{\alpha!\,\beta!\,\gamma!}\,\Pi^{\lambda\mu\nu}_{\alpha\beta\gamma}\ .\ .\ .\ .\ .\ .\ .\ .\quad (67')$$

Dies eingetragen in (65), (66) gibt für die zu beweisende Relation die Gestalt:

$$\left.\begin{aligned}
&\begin{vmatrix}
\mu_1 \Pi^{\lambda_1,\mu_1-1,\nu_1+1}_{p_1q_1r_1} - \nu_1 \Pi^{\lambda_1,\mu_1+1,\nu_1-1}_{p_1q_1r_1} \ldots \ldots \mu_3 \Pi^{\lambda_3,\mu_3-1,\nu_3+1}_{p_3q_3r_3} - \nu_3 \Pi^{\lambda_3,\mu_3+1,\nu_3-1}_{p_3q_3r_3} \\
\nu_1 \Pi^{\lambda_1+1,\mu_1,\nu_1-1}_{p_1q_1r_1} - \lambda_1 \Pi^{\lambda_1-1,\mu_1,\nu_1+1}_{p_1q_1r_1} \ldots \ldots \nu_3 \Pi^{\lambda_3+1,\mu_3,\nu_3-1}_{p_3q_3r_3} - \lambda_3 \Pi^{\lambda_3-1,\mu_3,\nu_3+1}_{p_3q_3r_3} \\
\lambda_1 \Pi^{\lambda_1-1,\mu_1+1,\nu_1}_{p_1q_1r_1} - \mu_1 \Pi^{\lambda_1+1,\mu_1-1,\nu_1}_{p_1q_1r_1} \ldots \ldots \lambda_3 \Pi^{\lambda_3-1,\mu_3+1,\nu_3}_{p_3q_3r_3} - \mu_3 \Pi^{\lambda_3+1,\mu_3-1,\nu_3}_{p_3q_3r_3}
\end{vmatrix} = \\
= &\begin{vmatrix}
r_1 \Pi^{\lambda_1\mu_1\nu_1}_{p_1,q_1+1,r_1-1} - q_1 \Pi^{\lambda_1\mu_1\nu_1}_{p_1,q_1-1,r_1+1} \ldots \ldots r_3 \Pi^{\lambda_3\mu_3\nu_3}_{p_3,q_3+1,r_3-1} - q_3 \Pi^{\lambda_3\mu_3\nu_3}_{p_3,q_3-1,r_3+1} \\
p_1 \Pi^{\lambda_1\mu_1\nu_1}_{p_1-1,q_1,r_1+1} - r_1 \Pi^{\lambda_1\mu_1\nu_1}_{p_1+1,q_1,r_1-1} \ldots \ldots p_3 \Pi^{\lambda_3\mu_3\nu_3}_{p_3-1,q_3,r_3+1} - r_3 \Pi^{\lambda_3\mu_3\nu_3}_{p_3+1,q_3,r_3-1} \\
q_1 \Pi^{\lambda_1\mu_1\nu_1}_{p_1+1,q_1-1,r_1} - p_1 \Pi^{\lambda_1\mu_1\nu_1}_{p_1-1,q_1+1,r_1} \ldots \ldots q_3 \Pi^{\lambda_3\mu_3\nu_3}_{p_3+1,q_3-1,r_3} - p_3 \Pi^{\lambda_3\mu_3\nu_3}_{p_3-1,q_3+1,r_3}
\end{vmatrix}
\end{aligned}\right\} \quad (69)$$

Mittels einiger Rekursionsformeln für Π bzgl. der oberen bzw. unteren Indizes beweist man leicht die für $\lambda + \mu + \nu = p + q + r$ gültigen Beziehungen:

$$\left.\begin{aligned}
r\,\Pi^{\lambda\mu\nu}_{p,q+1,r-1} - q\,\Pi^{\lambda\mu\nu}_{p,q-1,r+1} &= e_{11}\,\Omega_1 + e_{21}\,\Omega_2 + e_{31}\,\Omega_3 \\
p\,\Pi^{\lambda\mu\nu}_{p-1,q,r+1} - r\,\Pi^{\lambda\mu\nu}_{p+1,q,r-1} &= e_{12}\,\Omega_1 + e_{22}\,\Omega_2 + e_{32}\,\Omega_3 \\
q\,\Pi^{\lambda\mu\nu}_{p+1,q-1,r} - p\,\Pi^{\lambda\mu\nu}_{p-1,q+1,r} &= e_{13}\,\Omega_1 + e_{23}\,\Omega_2 + e_{33}\,\Omega_3
\end{aligned}\right\} \quad . \quad . \quad (70)$$

wo zur Abkürzung geschrieben ist:

$$\left.\begin{aligned}
\Omega_1 &= \mu\,\Pi^{\lambda,\mu-1,\nu+1}_{pqr} - \nu\,\Pi^{\lambda,\mu+1,\nu-1}_{pqr} \\
\Omega_2 &= \nu\,\Pi^{\lambda+1,\mu,\nu-1}_{pqr} - \lambda\,\Pi^{\lambda-1,\mu,\nu+1}_{pqr} \\
\Omega_3 &= \lambda\,\Pi^{\lambda-1,\mu+1,\nu}_{pqr} - \mu\,\Pi^{\lambda+1,\mu-1,\nu}_{pqr}
\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (70')$$

Sodann ergeben (70), der Produktsatz der Determinanten und die Orthogonalität der e_{ik} die Richtigkeit von (69), w.z.b.w.

Satz 3. Die Funktion G ist eine *P*-Funktion:

$$G_{1\ldots6} = G\begin{bmatrix} \lambda_1 \ldots \lambda_6 \\ \mu_1 \ldots \mu_6 \\ \nu_1 \ldots \nu_6 \end{bmatrix} \sim u_1^{\lambda_1}\, v_1^{\mu_1} \ldots w_6^{\nu_6}\,.$$

Beweis. Der Satz ist eine unmittelbare Folge der Hilfssätze 4, 5, 6, 7 und der LAPLACE-Zerlegung der Determinante (46).

Satz. 4. Die Funktion R ist eine P-Funktion:

$$R_{1\ldots 7} = R\begin{bmatrix} \lambda_1 \ldots \lambda_7 \\ \mu_1 \ldots \mu_7 \\ \nu_1 \ldots \nu_7 \end{bmatrix} \sim u_1^{\lambda_1} v_1^{\mu_1} \ldots w_7^{\nu_7}\,.$$

Beweis. Zunächst ändert man den Wert der Determinante (47) nicht, wenn in der 7ten Reihe die Gröszen $\dot{D}_{\lambda\mu\nu}$ durch $\frac{\partial D_{\lambda\mu\nu}}{\partial \bar{t}_{(\varepsilon)}}$ ersetzt werden. [vgl.: (11), (32), (36), (38)].

Sodann gilt für die letztere Grösze die Transformationsformel:

$$(60)\;\ldots\ldots\; \frac{\partial D_{\lambda\mu\nu}}{\partial \bar{t}_{(\varepsilon)}} = \sum_{(\alpha\beta\gamma)} \pi \begin{pmatrix} \lambda\ \mu\ \nu \\ \alpha\ \beta\ \gamma \end{pmatrix} \overline{\dot{D}}_{\alpha\beta\gamma} \;\ldots\ldots \quad (71)$$

Alsdann folgt Satz 4 aus (71), den Hilfssätzen 4, 5 und Satz 3.